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PRELIMINARY ASSESSMENT OF SUSPECTED CARCINOGENS IN DRINKING WATER

APPENDICES

ENVIRONMENTAL PROTECTION AGENCY

JUNE 1975

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(Appendices)

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16. ABSTRACT

This document contains detailed technical explanations of the research described briefly in the main report. The seven sections of the Appendix include presentation of the methodology and analysis of the National Organics Reconnaissance Survey; preliminary results of pilot plants to remove water contaminants; preliminary health effects assessment and other studies.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Drinking Water Contaminants, Suspected Carcinogens, Water Treatment Technology, Health Effects of Organic Contaminants, Water Pollution	Report to Congress, Safe Drinking Water Act, Suspected Carcinogens, Water Pollution	Report to Congress, Safe Drinking Water Act

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June 1975

TABLE OF CONTENTS

Page

I. Inventory of Organics Presently Identified in Drinking Water 1

II. National Organics Reconnaissance Survey 12

III. Organic Chemicals Found in Industrial Effluents 101

IV. Monitoring for Radiation in Drinking Water 123

V. Analysis of Inorganic Chemicals in Water Samples 129

VI. Preliminary Results of Pilot Plants to Remove Water Contaminants 147

VII. Health Effects Caused by Exposure to Drinking Water Contaminants 199

APPENDIX I

INVENTORY OF ORGANICS PRESENTLY IDENTIFIED IN DRINKING WATER

Prepared By

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Office of Research and Development
Cincinnati, Ohio

INVENTORY OF ORGANICS PRESENTLY IDENTIFIED IN DRINKING WATER

The following list of 187 compounds was compiled from an exhaustive search of the chemical literature and from EPA reports generated from the Agency's analytical activities. These compounds were identified from only a handful of public water supplies and do not constitute a definitive list of all compounds in all supplies. Because of the restrictive nature of the analytic systems employed to generate these identities, the list also is not inclusive of all compounds present in the water samples analyzed. These identifications represent the result of single or duplicate "grab" samples and, consequently, cannot be used to conclude continuous occurrence. Likewise, fluctuations in concentrations with time cannot be determined unequivocally from these same samples.

The terminology used in the list is not uniform because caution was taken to use the terminology employed by the investigator, regardless of the nomenclature system. For compounds identified by Water Supply Research Laboratory analysts, the chemical abstract names were assigned and used on the list.

The concentrations listed are to be considered minimum ranges. The values represent those reported by the analysts; however, in most cases, the values reflect concentrations in the extracted samples with extrapolation to the volume of water employed for the extraction. Since, for most quantification, the recovery data were not generated for the various extraction steps, the values must be considered minimum concentrations in the tap water samples analyzed.

This list of organics identified from potable water is being continuously updated, and information concerning the chemical properties and toxicity of these agents is being assembled and evaluated. Appendix VII(a) provides additional information about these compounds.

ORGANIC COMPOUNDS IDENTIFIED IN DRINKING WATER
IN THE UNITED STATES

(March 15, 1975)

	Compound	Range of Minimum Concentrations (μg/l)	References
1.	acenaphthene	-	5
2.	acenaphthylene	-	5
3.	acetaldehyde	-	24,30
4.	acetic acid	-	23
5.	acetone	-	1,2,7,20,24,30
6.	acetophenone	-	1
7.	acetylene dichloride	-	1
8.	aldrin	-	15
9.	atrazine	5.0	13,24
10.	desethyl atrazine	0.51	24
11.	barbital	-	14
12.	behenic acid, methyl ester	-	14
13.	benzaldehyde	-	25,31
14.	benzene	<5.0	1,2,7,23,26,28,31
15.	benzene sulfonic acid	-	15
16.	benzoic acid	-	5
17.	benzopyrene	-	12
18.	benzothiazole	-	3
19.	benzothiophene	-	5
20.	benzyl butyl phthalate	0.8	14,24
21.	bladex	-	25
22.	borneol	-	7,12,19
23	bromobenzene	-	1,2,7
24.	bromochlorobenzene	-	1,2,7,12
25.	bromodichloromethane	<5.0	6,20,22,23,24,26,27,28,30,31

26. bromoform	0.57-<5.0	1,6,24,26,28
27. bromoform butanal	-	23
28. bromophenyl phenyl ether	-	1,7
29. butyl benzene	-	1,2,7
30 butyl bromide	-	23
31. camphor	-	7,19
32. e-caprolactam	-	14
33. carbon dioxide	<5.0	26
34. carbon disulfide	-	24,30
35. carbon tetrachloride	5	1,2,23,24,28
36. chlordan(e)	-	15,25
37. chlordene	-	25
38. chlorobenzene	1-<5.0	1,2,7,23
39. 1,2-bis-chloroethoxy ethane	-	3
40. chloroethoxy ether	-	3
41. bis-2-chloroethyl ether	0.07-0.42	1,6,7,12,24,33
42. 2-chloroethyl methyl ether	-	12,14
43. chloroform	1.0-133	1,2,7,20,21,22,24,27,28,30,31
44. chlorohydroxybenzophenone	-	6
45. bis-chloroisopropyl ether	0.18-1.58	1,6,24,33
46. chloromethyl ether	-	7
47. chloromethyl ethyl ether	-	7
48. m-chloronitrobenzene	-	1,7,12
49. 1-chloropropene	<1.0	27
50. 3-chloropyridine	-	1,7
51. o-cresol	-	5
52. crotonaldehyde	5	31
53. cyanogen chloride	-	30
54. cycloheptanone	-	29
55. DDE	-	15
56. DDT	-	15,16
57. decane	0.04	23,24
58. dibromobenzene	-	23,24
59. dibromochloromethane	1.1-<5	6,20,23,24,27,28,31
60. dibromodichloroethane	0.33	24
61. di-t-butyl-p-benzoquinone	0.23	24

62. dibutyl phthalate	0.19	14,23,24
63. 1,3-dichlorobenzene	0.01	25
64. 1,4-dichlorobenzene	1.0	1,2,7,23
65. dichlorodifluoroethane	-	24
66. 1,2-dichloroethane	8.0	1,2,3,24,27,28
67. 1,1-dichloro-2-hexanone	<1	31
68. 2,4-dichlorophenol	36	5
69. dichloropropane	<1	27
70. 1,3-dichloropropene	<1	27
71. dieldrin	0.07-8.0	15,24,32
72. di-(2-ethylhexyl) adipate	0.003-0.31	25,31
73. diethyl benzene	<1	31
74. diethyl phthalate	0.03	14,24
75. di(2-ethyl hexyl) phthalate	0.31	14,24
76. dihexyl phthalate	0.03	24
77. dihydrocarvone	0.14	24
78. di-isobutyl carbinol	-	12
79. di-isobutyl phthalate	0.59	24
80. 1,2-dimethoxy benzene	-	1,7,19
81. 1,3-dimethylnaphthalene	-	1
82. 2,4-dimethyl phenol	-	5
83. dimethyl phthalate	0.27	24,25
84. dimethyl sulfoxide	-	1
85. 4,6-dinitro-2-aminophenol	-	5
86. 2,6-dinitrotoluene	-	1,7
87. dioctyl adipate	1.0-3.0	31
88. diphenylhydrazine	<1	31
89. dipropyl phthalate	0.14	24
90. docosane	-	14
91. n-dodecane	0.01	24
92. eicosane	-	14
93. endrin	0.004-0.008	15,24,25
94. ethanol	-	22,24,30,31
95. ethylamine	-	23
96. ethyl benzene	-	1,2,6,7

97. 2-ethyl-n-hexane	-	12
98. cis-2-ethyl-4-methyl-1,3-dioxolane	-	9,10
99. trans-2-ethyl-4-methyl-1,3-dioxolane	-	9,10
100. o-ethyltoluene	0.04	24
101. m-ethyltoluene	0.01-0.05	25
102. p-ethyltoluene	0.03	24
103. geosmin	-	4
104. heptachlor	-	15
105. heptachlor epoxide	-	15
106. 1,2,3,4,5,7,7-heptachloronorbornene	0.06	24
107. hexachlorobenzene	-	1
108. hexachloro-1,3-butadiene	0.06	15
109. hexachlorocyclohexane	-	15,16
110. hexachloroethane	4,4	6,24
111. hexachlorophene	0.01	11
112. hexadecane	-	14
113. 2-hydroxyadiponitrile	-	4
114. indene	-	5
115. isoborneol	-	7,11
116. isodecane	5.0	23
117. isophorone	2.9	24
118. 1-isopropenyl-4-isopropylbenzene	-	1
119. isopropyl benzene	-	2,7,12
120. limonene	0.03	24
121. p-meth-1-en-8-01	-	1,19
122. methane	-	34
123. methanol	-	24
124. 2-methoxy biphenyl	-	1
125. o-methoxy phenol	-	1,7,19
126. methyl benzoate	-	24
127. methyl benzothiazole	-	3
128. methyl biphenyl	-	1
129. 3-methyl butanal	-	24,29
130. methyl chloride	-	1,2,7
131. methylene chloride	<5	2,20,26,30,31

132. methyl ethyl benzene	<1	31
133. methyl ethyl ketone	-	23,24,25
134. 2-methyl-5-ethyl-pyridine	-	12
135. methylindene	-	12
136. methyl methacrylate	<1.0	31
137. methyl naphthalene	-	12
138. methyl palmitate	-	14
139. methyl phenyl carbinol	-	12
140. 2-methylpropanal	-	24,30
141. methyl stearate	-	14
142. methyl tetracosanoate	-	14
143. naphthalene	1.0	5,23
144. nitroanisole	-	1,11
145. nitrobenzene	-	1,7
146. nonane	0.03-10.0	23,24
147. octadecane	-	3
148. octane	-	14
149. octyl chloride	-	23
150. pentachlorobiphenyl	-	14
151. pentachlorophenol	0.06	18
152. pentachlorophenyl methyl ether	-	25
153. pentadecane	0.02	24
154. pentane	-	3
155. pentanol	1.0	23
156. phenyl benzoate	-	14
157. phthalic anhydride	-	14
158. piperidene	-	23
159. propanol	1.0	23,30
160. propazine	-	25
161. propylamine	-	23
162. propylbenzene	<5	26
163. simazine	-	25
164. 1,1,3,3-tetrachloroacetone	-	14
165. tetrachlorobiphenyl	-	14
166. 1,1,1,2-tetrachloroethane	0.11	23,24,25
167. tetrachloroethylene	0.41-<5.0	24,27,28

168. tetradecane	-	24
169. tetramethyl benzene	<1.0	31
170. thiomethylbenzothiazole	-	3
171. toluene	1.0-<5.0	1,2,3,6,7,23,24,26
172. trichlorobenzene	1.0	23
173. trichlorobiphenyl	-	14
174. 1,1,2-trichloroethane	-	1,7,24,28
175. 1,1,2-trichloroethylene	<1.0	24,27
176. trichlorofluoromethane	-	28
177. 2,4,6-trichlorophenol	-	14
178. n-tridecane	0.12	24
179. trimethyl benzene	<5.0	26,31
180. 3,5,5-trimethyl-bicyclo (4,1,0) heptene-2-one	-	29
181. trimethyl-trioxo-hexadydro-triazine	-	24
182. triphenyl phosphate	-	24
183. n-undecane	0.02	24
184. vinyl benzene	-	1,2,6,7,31
185. o-xylene	<5.0	6,25,26,31
186. m-xylene	0.05-<5.0	26
187. p-xylene	<5.0	26

REFERENCES

1. Industrial Pollution of the Lower Mississippi River in Louisiana. U. S. Environmental Protection Agency, Region VI, Dallas, Texas. Surveillance and Analysis Division, April 1972.

2. Progress Report: Identification of Hazardous Materials, Lower Mississippi River Basin. U. S. Department of Interior, Federal Water Quality Administration, Lower Mississippi River Basin Field Station, October 1970.

3. Burnham, A. K., Calder, G. V., Fritz, J. S., Junk, G. A., Svec, H. J. and Vick, R. Trace organics in water: their isolation and identification. Journal American Water Works Assn. 65(11): 722-25, 1973. Iowa State University, Ames, Iowa.

4. Deinzer, Max. Informal memorandum - Recovery from Merrimac River, Lawrence, Massachusetts. WSRL, NERC-Cinti., Dec. 1972.

5. Burnham, A. K., Calder, G. V., Fritz, J. S., Junk, G. A., Svec, H. J. and Willis, R. Identification and estimation of neutral organic contaminants in potable water. Anal. Chem. 44(1):139-41, 1972

6. Kleopfer, Robert D. and Fairless, Billy J. Characterization of organic components in municipal water supply. Environ. Sci. and Tech. 6:1036, Nov. 1972.

7. Friloux, James (Acting Chief). Petrochemical wastes as a water pollution problem in the Lower Mississippi River. Lower Mississippi Basin Office, Water Quality Office, EPA, Baton Rouge, Louisiana, Oct. 1971. (Submitted to Senate Subcommittee on air and water pollution, New Orleans, Louisiana - April 5, 1971.)

8. Tardiff, Robert G. and Deinzer, M. Toxicity of organic compounds in drinking water. Proceedings of 15th Water Quality Conference, Feb. 7-8, 1973, University of Illinois, pp.23-27.

9. Finger, James H. Chemical Services Branch, Region IV, EPA, Surveillance and Analysis Division, March 16, 1973. Correspondence to W. Bowman Crum, Jr. of Water Pollution Control Division, South Carolina Pollution Control Authority, Columbia, S. Carolina 29211.

10. Finger, James H. Chemical Services Branch, Region IV, EPA Surveillance and Analyses Division, March 16, 1973. Correspondence (to) Thos. C. Kurimcak, S. Carolina State Board of Health, Columbia, S. Carolina.

11. Buhler, Donald R., Rasmusson, M. E. and Nakahue, H. S. Occurence of hexachlorophene and pentachlorophenol in sewage and water. Envir. Sci. and Tech. 7(10):929-34, Oct. 1973.

12. Miller, S. S. (Mg. Ed.). Are you drinking biorefractories, too? Env. Sci and Tech. 7:14, 1973

13. Kleopfer, Robert D., Kansas (Region VII). Correspondence (to) Dr. L. E. Harris, NERC-Cincinnati, Sept. 19, 1973. EPA-Mass Spectrometer Users' Group Newsletter #5, Sept. 1973.

14. Deinzer, M., Melton, R., Mitchell, D., Kopfler, F. and Coleman, E. Trace organic contaminants in drinking water; their concentration by reverse osmosis. Presented to Division of Environmental Chemistry, A. C. S., Los Angeles, Calif., March 1974.

15. Schafer, M. L., Peeler, J. T., Gardner, W. S., Campbell, J. E. Pesticides in drinking water: water from the Mississippi and Missouri Rivers. Env. Sci. Tech. 3(12):1261, 1969.

16. West, I. Pesticides as contaminants. Arch. Environ. Health 9:626, 1964.

17. Weibel, S. R., Weidner, R. B., Cohen, J. M. and Christianson, A. G. Pesticides and other contaminants in rainfall and runoff. JAWWA 58(8):1075, 1966.

18. Young, Clarence L. California Department of Health. Memo March 22, 1974 (to) Henry Ongerth and Dr. Alice Ottoboni. Cellon treated wood - pentachlorophenol - reservoir covers.

19. Alford, Ann L. Environmental Applications of Advanced Instrumental Analysis: Assistance Project, FY-72. (EPA 660/2-73-013) NERC, Corvallis, Oregon. Washington, D. C., G. P. O., 1973.

20. Melton, R. (Task 05) Application of mass spectrometry and NMR spectroscopy to identification of organics in drinking water. NERC-Cincinnati Quarterly Report for April-June 1974.

21. Kleopfer, Robert D. Kansas (Region VII). Correspondence (to) Dr. W. L. Budde, NERC-Cinti. (Halogenated methanes.) February 12, 1974.

22. Bellar, T. A., Lichtenberg, J. J., and Kroner, R. C. The occurrence of organohalides in finished drinking waters. MDQRL, NERC-Cincinnati, JAWWA 66:739, 1974.

23. Scheiman, M. A., Saunders, R. A., and Saalfeld, F. E. Organic contaminants in the District of Columbia water supply. Chemistry Division, Naval Research Laboratory, Washington, D. C., 1974. (Submitted to J. of Biomedical Mass Spectrometry.)

24. New Orleans Area Water Supply Study. (Draft Analytical Report) Lower Mississippi River Facility, Slidell, Louisiana, November 1974.

25. Garrison, Arthur W. Technical Assistance Summary: Analysis of New Orleans Drinking Water. EPA Region VI, Task TA 75-03, November 1974.

26. Saunders, R. A., Blackly, C. H., Kovacina, T. A., Lamontagne, R. A., Swinnerton, J. W., Saalfeld, F. E. Identification of volatile organic contaminants in Washington, D. C. municipal water. Naval Research Laboratory, Washington, D. C. 20375.

27. Dowty, Betty; Carlisle, Douglas; and Laseter, John L. Halogenated hydrocarbons in New Orleans water and blood plasma. Science 187 (4171):75-77, Jan. 10, 1975.

28. Melton, R. G. Task 006. Chemical characterization of organics in tap water and tap water concentrates. WSRL, NERC-Cincinnati Quarterly Report, October-November 1974.

29. Lee, Ramon G. EPA Region III. Correspondence to R. W. Ludlow, Jr., Department Health and Mental Hygiene, Baltimore, Md. about low levels of organic compounds analyzed in Annapolis water supply. Jan. 21, 1975.

30. Melton, R. G. and Coleman, Emile. Internal (EPA) memo to Earl McFarren. GC-MS analysis of White House water. (D. C. Water Supply.) Feb. 4, 1975.

31. Snyder, Daniel J., III. EPA Regional Administrator Water Supply Analysis. Press Release delivered at Allegheny Board of Health, January 30, 1975.

32. Thomas, R. F. Identification of organophosphorus compound in water. Environmental Protection Agency, Mass Spectrometer Users' Group Newsletter #14, February 1975, Cincinnati, Ohio 45268.

33. Dressman, R. C. and McFarren, E. F. Detection and measurement of bis(2-chloro-)ethers and dieldrin by gas chromatography. Presented at the 2nd Annual Water Quality Technology Conference of the American Water Works Association, Dallas, December 1-4, 1974.

34. Nordell, E. Water Treatment for Industrial and Other Uses. New York, Reinhold Publishing Corp., 1961.

APPENDIX II

NATIONAL ORGANICS RECONNAISSANCE SURVEY

Table of Contents

Page

A. Objectives 18

B. Selection of Cities 18

C. Procedure 18

  1. Engineering Evaluation of Treatment Facilities 18

  2. Sampling 20

    a. Selected Organic Compounds 20

      1) Trihalomethanes, Carbon Tetrachloride, 1,2-Dichloroethane 20

      2) Polychlorinated biphenyls, Haloethers and Organophosphate pesticides 21

      3) Vinyl chloride 21

    b. General Organic Parameters 21

      1) Non-volatile Total Organic Carbon, Ultraviolet Absorption, Fluorescence 21

    c. Comprehensive Organics Analyses 22

      1) Organics Purged from Sample 22

      2) Organics Extracted from Sample with Solvent 22

      3) Organics Adsorbed on Activated Carbon from Sample 22

Page

d. Constituents in Drinking Water Regulations 24

1) Inorganics 24

2) Organics - Carbon Adsorbables (CCE-m) 24

3) Pesticides (chlorinated hydrocarbons) and Herbicides 24

3. Analytic Methods 25

a. Selected Organic Compounds 25

1) Chloroform, Bromodichloromethane, Dibromochloromethane, Bromoform, Carbon Tetrachloride, 1,2-Dichloroethane 25

2) Polychlorinated biphenyls 29

3) Bis-(2-chloroethyl) ether, Bis-(2-chloroisopropyl) ether 29

4) Vinyl chloride 29

5) Organophosphate Pesticides 30

b. General Organic Parameters 30

1) Non-volatile Total Organic Carbon 30

2) Ultraviolet Absorption 30

3) Fluorescence 30

c. Comprehensive Organic Analyses 30

1) Organics Purged from Sample 31

2) Organics Extracted from Sample with Solvent 36

3) Organics Adsorbed on Activated Carbon from Sample 38

d. Constituents in Drinking Water Regulations 40

1) Inorganics 40

2) Organics - Carbon Adsorbable (CCE-m) 40

Page

3) Pesticides (chlorinated hydrocarbons), 2,4-D and Silvex 40

4. Quality Control 42

D. Results 42

1. Source and Treatment Information 44

2. Data from 80 Location Survey 44

a. Raw Water Data 44

b. Finished Water Data 46

1) Organics 46

2) Inorganics 46

3. Confirmation Samples 46

a. Quantitative 46

b. Qualitative 69

4. Comprehensive 5-Location Study 69

a. Groundwater, Miami, Florida 69

1) Selected Compound Analysis 69

2) Organics Purged from Sample 70

3) Organics Extracted from Sample with Solvent 70

4) Organics Adsorbed from Sample by Activated Carbon 70

b. Uncontaminated Upland Water, Seattle, Washington . . 73

1) Selected Compound Analysis 73

2) Organics Purged from Sample 73

3) Organics Extracted from Sample with Solvent . . 73

4) Organics Adsorbed from Sample by Activated Carbon 74

Page

c. Raw Water Contaminated by Agricultural Runoff, Ottumwa, Iowa 74

1) Selected Compound Analysis 74

2) Organics Purged from Sample 75

3) Organics Extracted from Sample with Solvent . . 75

4) Organics Adsorbed from Sample by Activated Carbon 76

d. Raw Water Contaminated by Municipal Discharges, Philadelphia, Pennsylvania 76

1) Selected Compound Analysis 76

2) Organics Purged from Sample 78

3) Organics Extracted from Sample by Solvent . . . 78

4) Organics Adsorbed from Sample on Activated Carbon 78

e. Raw Water Contaminated with Industrial Discharges, Cincinnati, Ohio 79

1) Selected Compound Analysis 79

2) Organics Purged from Sample 79

3) Organics Extracted from Sample by Solvent . . . 79

4) Organics Adsorbed from the Sample on Activated Carbon 79

E. Discussion 82

1. Are Trihalomethanes Formed by Chlorination and, If So, How Widespread Is Their Occurrence? 82

a. Trihalomethanes 82

b. 1,2-Dichloroethane and Carbon Tetrachloride 82

c. Non-Volatile Total Organic Carbon 82

Page

2. Influence of Source Type and Treatment Practice on Trihalomethane Formation 84
    a. Source Influence 86
    b. Treatment Influence 87
        1) Chlorination Practice 87
        2) Filtration Practice 88
        3) Use of Activated Carbon 88
            A. Powder 88
            B. Granular 88
    c. Section Summary 91
3. Alternate Indicators of Organic Contaminant Levels . . . 92
4. Organics Found in the 5-Location Study 94
5. Significance of Findings 94

F. Acknowledgements 98

G. References 99

NATIONAL ORGANICS RECONNAISSANCE SURVEY

A. OBJECTIVES

The National Organics Reconnaissance Survey has three major objectives. One, is to determine the extent of the presence of the four trihalomethanes, chloroform, bromodichloromethane, dibromochloromethane, and bromoform in finished water, and to determine whether or not these compounds are created by chlorination. A second objective is to determine what effect raw water source, and other water treatment practices have on the formation of these compounds, if they are formed by chlorination. The third objective is to characterize, as completely as possible using existing analytic technology, the organic content of finished drinking water produced from raw water sources representing the major categories in use in the United States today.

B. SELECTION OF CITIES

For the study of the formation of chlorination by-products, 80 water supplies were chosen to participate in the NORS in consultation with State water supply officials. These 80 supplies were geographically distributed, some being in each of the U.S. EPA's 10 Regions. The supplies were chosen to represent as wide a variety of raw water sources and treatment techniques as possible. Table 1 lists the names of the 80 supplies chosen.

Ten of the 80 cities below were chosen as sites for a more comprehensive survey of the organic content of the finished water. These locations were chosen to represent five major categories of raw water sources. These were: 1) ground water; 2) uncontaminated upland water; 3) raw water contaminated with agricultural runoff; 4) raw water contaminated with municipal waste; and 5) raw water sources contaminated with industrial discharges. Table 2 lists these ten cities by category.

C. PROCEDURE

1. Engineering Evaluation of Treatment Facilities

At each of the 80 sites chosen for study, engineers from the U.S. EPA Regional Office visited the water treatment plant and evaluated the facilities. They collected basic information on the raw water source and treatment facilities, which are enclosed in this report. In addition to this information these engineers also determined the dosage of various water treatment chemicals used and their points of application.

TABLE 1

1. Lawrence, Massachusetts
2. Waterbury, Connecticut
3. Boston, Massachusetts (MDC)
4. Newport, Rhode Island
5. New York, New York
6. San Juan, Puerto Rico
7. Passaic Valley Water Commission, New Jersey
8. Tom's River, New Jersey
9. Buffalo, New York
10. Rhinebeck, New York
11. Philadelphia, Pennsylvania
12. Wilmington Suburban, Delaware
13. Newark, Delaware (Artesian Water Co.)
14. Washington, District of Columbia
15. Baltimore, Maryland
16. South Pittsburgh, Pennsylvania
17. Strasburg, Pennsylvania
18. Fairfax County Water Authority, Virginia
19. Hopewell, Virginia
20. Huntington, West Virginia
21. Wheeling, West Virginia
22. Miami, Florida
23. Jacksonville, Florida
24. Atlanta, Georgia
25. Owensboro, Kentucky
26. Greenville, Mississippi
27. Chattanooga, Tennessee (Tennessee American Water Company)
28. Memphis, Tennessee
29. Nashville, Tennessee
30. Charleston, South Carolina
31. Cincinnati, Ohio
32. Chicago, Illinois
33. Clinton, Illinois
34. Indianapolis, Indiana
35. Whiting, Indiana
36. Detroit, Michigan
37. Mt. Clemens, Michigan
38. St. Paul, Minnesota
39. Cleveland, Ohio
40. Columbus, Ohio
41. Dayton, Ohio
42. Indiana Hill, Ohio
43. Piqua, Ohio
44. Youngstown (Mahoning Valley San. Dist.)
45. Milwaukee, Wisconsin
46. Oshkosh, Wisconsin
47. Terrebonne Parish, Louisiana
48. Camden, Arkansas
49. Logansport, Louisiana
50. Albuquerque, New Mexico
51. Oklahoma City, Oklahoma
52. Brownsville, Texas
53. Dallas, Texas
54. San Antonio, Texas
55. Ottumwa, Iowa
56. Clarinda, Iowa
57. Davenport, Iowa
58. Topeka, Kansas
59. Cape Girardeau, Missouri
60. Kansas City, Missouri
61. St. Louis County, Missouri
62. Lincoln, Nebraska
63. Grand Forks, North Dakota
64. Denver, Colorado
65. Pueblo, Colorado
66. Huron, South Dakota
67. Salt Lake City, Utah
68. Phoenix, Arizona
69. Tucson, Arizona
70. California Water Project at Coalinga, California
71. Contra Costa County Water District, California
72. Dos Palos, California
73. Los Angeles, California (Owens Aqueduct)
74. San Diego, California (Colorado River Aqueduct)
75. San Francisco, California
76. Seattle, Washington
77. Douglas, Alaska
78. Idaho Falls, Idaho
79. Corvallis, Oregon
80. Illwaco, Washington

TABLE 2

Ground Water

1) Miami, Florida
2) Tucson, Arizona

Uncontaminated Upland Water

1) Seattle, Washington
2) New York, New York

Contamination by Agricultural Runoff

1) Ottumwa, Iowa
2) Grand Forks, North Dakota

Contamination by Municipal Waste

1) Philadelphia, Pennsylvania
2) Terrebonne Parish, Louisiana

Contamination by Industrial Discharges

1) Cincinnati, Ohio
2) Lawrence, Massachusetts

1 = First Series, sampled in early 1975.

2 = Second Series, to be sampled in the future.

2. Sampling

a. Selected Organic Compounds

1) Trihalomethanes, Carbon Tetrachloride, 1,2-Dichloroethane

Because the six compounds chosen for study were known to be volatile, a sampling procedure was chosen that would provide for minimum loss of the six compounds from the water to the atmosphere while the sample was in shipment or awaiting analysis by the technique of volatile organic analysis (VOA) (see Section C(3)(2)(1) for analytic technique).

The containers chosen were glass 50-ml "Hypo-Vials"* sealed with Teflon faced "Tuf-Bond" discs, both available from Pierce Chemical Co.,

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*Mention of commercial products does not constitute endorsement by U.S. EPA.

Rockford, Ill. Prior to use, the glass vials were capped with aluminum foil and muffled at 400°C for at least one hour to destroy or remove any organic matter interfering with analysis. The bottles were packed, aluminum foil still in place, along with sufficient discs and aluminum seals (to secure the discs in place), labels and re-usable ice packs in an insulated container, and shipped to the appropriate regional office for sampling. Sufficient materials were provided for taking three raw- and three finished-water samples.

In the field the vials were filled bubble-free, to overflowing so that a convex meniscus formed at the top. The excess water was displaced as the disc was carefully placed, teflon side down, on the opening of the vial. The aluminum seal was then placed over the disc and the neck of the vial and crimped into place. A sample taken and sealed in this manner was completely headspace-free at the time of sampling. Usually a small bubble would form during shipping and storage, however.

The samples were labeled appropriately, repacked with the frozen ice packs in the original insulated container and returned via air mail to the Water Supply Research Laboratory in Cincinnati. After receipt at the laboratory, the samples were refrigerated until analyzed. Samples were collected from the 80 locations during the period late January to end of March 1975.

2) Polychlorinated biphenyls, Haloethers, Organophosphate Pesticides

Samples were collected in glass gallon jugs that had been detergent washed, tap water rinsed and muffled at 400°C for 15 minutes in an ultra high temperature oven. Caps were teflon lined. Samples were received over a period of one month, late January to late February 1975 from the First Series of the comprehensive analyses locations (Table 2) and were refrigerated until all could be extracted at the same time.

3) Vinyl chloride

Samples for vinyl chloride in raw and finished water were collected using the same procedure described in Section C(2)(a)(1) during the period from the end of January through the end of February 1975 from the First Series of the comprehensive analysis locations (Table 2).

b. General Organic Parameters

1) Non-volatile Total Organic Carbon, Ultraviolet Absorption, Fluorescence

One of the sealed bottles of both raw and finished water described in in Section C(2)(a)(1), collected from all 80 locations, was used as the sample for these three parameters.

c. Comprehensive Organic Analyses

1) Organics Purged from Sample

All samples were collected from a potable water tap in one predetermined water plant of each study city (First Series - Table 2). With the exception of Ottumwa, Iowa, the samples for comprehensive volatile organics analyses were taken from the same tap as the samples for other organic analyses in the NORS. Samples were collected between the last of January through the last of February 1975. Prior to sampling, the tap water was allowed to run at a maximum discharge rate for 15 minutes. During sampling, the discharge rate was adjusted to avoid agitation of the sample. All samples were collected in glass serum bottles previously muffled at 550°C for 4 hours, were capped with teflon lined discs, and were sealed with aluminum caps, as described in Section C(2)(a)(1). The vials containing samples collected for comprehensive volatile organic analyses were filled completely so that no air would be present; whereas, those for head gas analyses were filled to within 1/4 inch of the disc to allow the escape of volatiles into the head space. Samples were stored and shipped at 4°C and were analyzed 24 to 168 hours after collection.

2) Organics Extracted from Sample with Solvent

Samples were collected in glass gallon jugs that had been detergent washed, tap water rinsed and muffled at 400°C for 15 minutes in an ultra high temperature oven. Caps were teflon lined. Samples were received over a period of one month, late January to late February 1975 from the First Series of the comprehensive analyses locations (Table 2) and were refrigerated until all could be extracted at the same time.

3) Organics Adsorbed on Activated Carbon from Sample

A low flow CAM sampling train was used in the First Series of the comprehensive analyses locations (Table 2). Each unit consisted of two 3" diameter pyrex glass columns packed with Filtrasorb 300 granular activated carbon, a teflon-stainless rotameter for flow rate control, and a volume measuring device to count the liters that passed through the carbon columns (see Figure 1). The end plates, fittings and valves were stainless steel. The gaskets and tubing that contacted the water sampled were teflon or stainless steel. Prior to use in the field the pyrex glass columns were detergent washed, then muffled in an oven at 400°C for 15 minutes to render them organic free. The units were then placed into operation by connecting them to a finished water tap at the site sampled and flushing the fines from the activated carbon columns with twenty liters of finished water.

The units were then operated, with continuous flow, 24 hours a day for seven days at a rate of approximately 600 ml/min. The time of sampling and flow rate were selected to result in the passage of at least 6000 liters of finished water through the two columns. Because of

LEGEND:

1. TEFLON TUBING
2. STAINLESS STEEL AND TEFLON ROTAMETER
3. STAINLESS STEEL TUBING
4. STAINLESS STEEL VALVE
5. TEFLON GASKETS, STAINLESS STEEL SCREENS AND END PLATES
6. 18" LONG x 3" DIAMETER PYREX COLUMN PACKED WITH FILTRASORB 300 ACTIVATED CARBON
7. VOLUME MEASUREMENT CONTROL
8. COUNTER

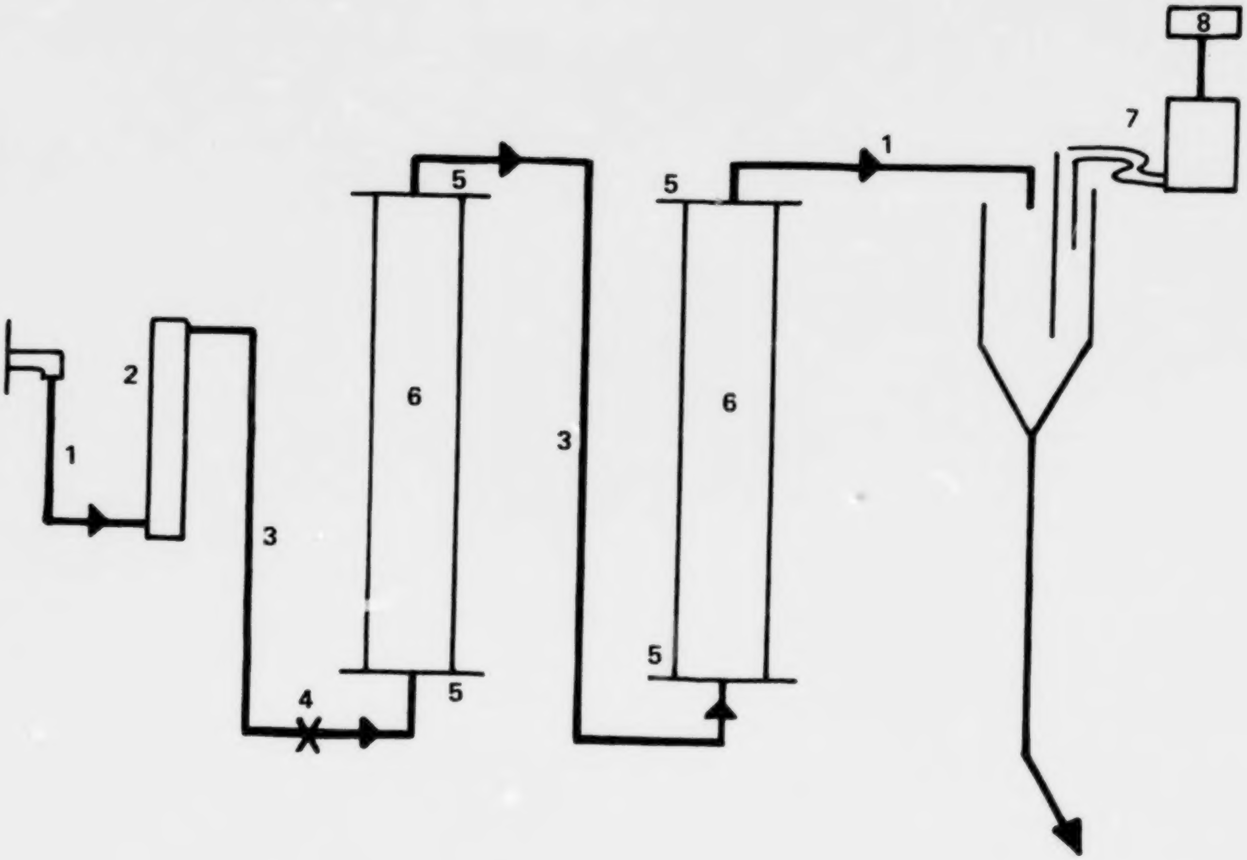

FIGURE 1. CARBON ADSORPTION MONITORING UNIT

difficulties with this procedure the 5 locations were sampled in early April 1975, rather than in February, when the other samples were taken.

d. Constituents in Drinking Water Regulations

1) Inorganics

Four one-quart plastic cubitainers of water were collected at the same place, and at approximately the same time, so as to represent essentially one sample. Each was identified by writing the same serial number on the container. To assist the analyst, each container was also identified by writing on the outside the preservative added, i.e., no preservative, HNO_3, $HgCl_2$ or NaOH. The amount of preservative added to each quart cubitainer and the analyses carried out on each of the particularly preserved samples is as follows:

1. Trace metals - 1-1/2 ml of concentrated nitric acid.
2. Nitrates, and methylene blue active substances - 1 ml of a 20,000 mg/l solution of mercury (2.21 g $HgCl_2$ per 100 ml).
3. Cyanide - 1-1/2 ml of 2 N sodium hydroxide.
4. Turbidity, color, pH, chloride, sulfate, fluoride, specific conductance, and total dissolved solids - no preservative added.

These samples were collected from all 80 locations from the last week in January through March 1975.

2) Organics - Carbon Adsorbable (CCE-m)

The sampler and sampling techniques described in Reference 1 were used to collect samples for carbon-chloroform extract (CCE-m). These samples were collected at the First Series of locations listed in Table 2 from the last week in January through the last week in February 1975.

3) Pesticides (chlorinated hydrocarbons) and Herbicides

These analyses were performed on the sample referred to in Section C(2)(a)(2).

3. Analytic Methods

a. Selected Organic Compounds

1) Chloroform*, Bromodichloromethane*, Dibromochloromethane*, Bromoform*, Carbon Tetrachloride**, 1,2-Dichloroethane***

Part I, Routine Analysis. The sample concentration procedure chosen for the initial step of identification and measurement of the six volatile halogenated organics was essentially that of Bellar and Lichtenberg.[2] In this procedure, the sample is purged with an inert gas that is passed, in series, through an adsorbant material that traps and concentrates the organic materials of interest. The organics are then desorbed from the trapping material by heating under a gas flow and transferred thusly to the first few millimeters of a cold gas chromatography (GC) column. Separation (chromatography) is then carried out with temperature programming.

During this survey, only single column GC was routinely performed, mostly because of the shortness of time for completion of the NORS. A high level of confidence that proper identifications were made was attained by use of the Hall Electrolytic Conductivity Detector operated in the specific halogen mode. Further assurance of proper identifications was given by supplementary analysis of 9 each, raw- and finished-duplicate water pairs (from selected locations) on a second column using a microcoulometric detector operated in the oxidative halogen mode. Finally, the qualitative results of analysis of 15 of the finished water samples were confirmed by GC/MS analysis (see Part II of this Section).

Apparatus. The glass purging device and stainless steel traps used in the analyses were fabricated exactly according to Bellar and Lichtenberg.[2] The adsorbant material used in the trap was Tenax-GC, 60/80 mesh (Applied Science, State College, Pa., or Alltech Associates, Arlington Heights, Ill.)

The chromatograph used for analysis was a Varian Model 2100 with one inlet modified to the general configuration of Bellar and Lichtenberg's desorber Number 1. The column used for separation of the six compounds was 12 ft x 2 mm I.D. glass, packed with Tenax GC, 60/80 mesh. The column effluent was connected via a stainless steel transfer line to a Tracor Model 310 Hall Electrolytic Conductivity Detector (Tracor, Inc., Austin, Texas) for detection and measurement of the compounds. This detector was chosen as the most suitable for the immediate needs of the survey.[3]

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*Selected as possible chlorination by-products.
**Selected because of known effect on health.
***Selected because presence in previously sampled finished waters.

Reagents. Blank water and water used for dilution of standards was prepared by purging distilled water with helium until no interfering peaks could be detected by use of the complete analytical procedure.

Stock standards were prepared with dilutions of 95% ethanol of the test compounds. The appropriate final aqueous dilution was made by 1-10 µg/l injection of an appropriate stock standard directly through the valve on the 5-ml sampling syringe (see description below) into a blank water contained therein.

Procedure. The sealed water sample as received from the field, was heated to 25°C in a water bath. Just prior to the actual analysis, the entire disc-seal combination cap was removed with a "Dekapitator" (Pierce Chemical Co.). Duplicate aliquots from the sample were each taken as follows: A glass 5-ml Luer-Lok syringe (plunger removed) was fitted at the tip with a closed Luer-Lok one-way brass stopcock. The water sample was poured into the back of the barrel of the syringe until the barrel was completely full. The plunger was then quickly inserted into the barrel in such a way as to eliminate air bubbles. The valve was opened momentarily. The plunger was depressed to the 5 ml mark to expel excess sample, whereupon the valve was again closed. Only one of these aliquots was routinely analyzed; the duplicate was simply stored in this configuration until the success of the first analysis was assured.

The syringe assembly containing the aliquot to be analyzed was connected to the Luer-Lok needle that was inserted into the sample inlet of the purging device (the needle was never withdrawn from the septum). At the time of analysis the valve was opened and the sample was expelled from the syringe by depressing the plunger. After this, the valve was closed until purging was complete. After purging, the water (to be discarded) was removed by reversing the above procedure.

The technique of purging the sample and desorption of the trap contents onto the GC column were carried out exactly as described by Bellar and Lichtenberg. Purging was for 11 minutes with a helium gas flow of 20 ml per minute. Desorption was for three minutes at 180°C with a flow of helium through the trap onto the GC column of 20 ml per minute (this was in addition to the carrier gas flow). At this time, the GC column was at room temperature.

Separation of the compounds was accomplished by first quickly heating the column to 95°C, following with a 15-minute hold, then programming at 2°C per minute to a final temperature of 180°C with a helium carrier flow of 20 ml per minute. Conditions for operation of the detector were those recommended by the manufacturer for optimum performance in the halogen mode.

Compounds were identifided according to retention time (measured from beginning of the hold at 95°C) and quantified by comparison of peak heights relative to standards prepared at similar concentration.

Retention data and the range of minimum quantifiable concentrations (MQC) encountered for the six compounds during the survey are summarized in Table 3.

TABLE 3

CHROMATOGRAPHIC RETENTION AND SENSITIVITY DATA

Compound	Typical Retention Time (min.)	Minimum Quantifiable Concentration (MQC)**, µg/l range obs. during survey
$CHCl_3$	20.3	0.1 - 0.2
$(CH_2Cl)_2$	25.8	0.2 - 0.4
CCl_4	27.7*	1.0 - 2.0
$CHBrCl_2$	31.8	0.2 - 0.8
$CHBr_2Cl$	41.2	0.4 - 2.0
$CHBr_3$	49.7	1.0 - 4.0

Retention times given were typical. They varied slightly with aging of the columns and significantly with installation of a replacement column. MQC was not constant throughout the study because of various changes in normal operating parameters. No attempt was made to standardize the MQC; operational parameters were simply adjusted to the optimum for any given day.

Part II, Confirmation Analysis. As noted above, to add confidence to the routine analysis for the six chosen volatile halogen containing organics, replicate samples from selected locations were subjected to reanalysis for quantitation on a second GC-Detector system and for qualitative analysis with a GC/MS system. Table 4 shows the sampling locations of these confirmation samples.

Quantitative Analysis

The quantitative analysis was similar to Reference 2. The following details describe the specific procedure.

Storage. All samples were stored at 4°C until just prior to analysis.

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*Broad peak not completely resolved from $(CH_2Cl)_2$.
**2% scale deflection.

TABLE 4

Quantitative Confirmation

1. Waterbury, Connecticut
7. Passaic Valley Water Commission, New Jersey
16. South Pittsburgh, Pennsylvania
30. Charleston, South Carolina
51. Oklahoma City, Oklahoma
60. Kansas City, Missouri
65. Pueblo, Colorado
71. Contra Costa County Water District, California
79. Corvallis, Oregon

Qualitative Confirmation

11. Philadelphia, Pennsylvania
21. Wheeling, West Virginia
22. Miami, Florida
30. Charleston, South Carolina
31. Cincinnati, Ohio
41. Dayton, Ohio
51. Oklahoma City, Oklahoma
55. Ottumwa, Iowa
58. Topeka, Kansas
60. Kansas City, Missouri
66. Huron, South Dakota
71. Contra Costa County Water District, California
72. Dos Palos, California
76. Seattle, Washington
79. Corvallis, Oregon

Extraction. Five ml of each sample was purged for 11 minutes with nitrogen flowing at 20 ml/min. The purging device was maintained at 19°C. The sample was introduced into the purging device at 4°C. Therefore, as the sample was purged it warmed up to 19°C at an unknown rate.

Concentration. The sample was concentrated using a trap packed with 18 cm of Davison silica gel, grade 15, 35-60 mesh. Desorption took place for 4.0 minutes at 200°C.

Analytic Procedure. An Infotronics Model 2400 gas chromatograph equipped with a Dohrman microcoulometric detector (halide specific mode, oxidative) was used to perform the analyses.

A stainless steel column packed with Porasil-C coated with Carbowax-400, 100/120 mesh, 6' long, 0.1 inch I.D. was used to perform the separations. Nitrogen flowing at 50 ml/minute was employed as the carrier gas. The column was programmed over the following conditions: 1) Desorb into column for four minutes at <30°C; 2) heat column to 50°C and hold one minute; and 3) program column to 175°C at 8°/minute.

Using the above mentioned conditions the limit of detection for the materials of interest were: chloroform, 0.05 µg/l; bromodichloromethane, 0.1 µg/l; dibromochloromethane, 0.1 µg/l; bromoform, ∿5 µg/l; 1,2-dichloroethane, 0.1 µg/l; and carbon tetrachloride, 0.05 µg/l. Methylene chloride was routinely detected; the limit of detection was 0.05 µg/l. Other unknown organohalides were detected; unfortunately their concentrations were below the limit of detection for GC/MS identification. By calculating relative retention times it was found that the same unknown organohalides were present in many of the water supplies tested.

Qualitative Analysis - GC/MS

A Varian aerograph 1400 gas chromatograph with a Finnigan 1015C quadrupole mass spectrometer controlled by a Systems Industries 150 data acquisition system was used to perform the analyses. A glass column packed with Porasil-C coated with Carbowax-400, 100/120 mesh, 6' long x 2 mm I.D. was used to perform the separations. Helium at 30 ml/min was used as the carrier gas. The column was programmed under the following conditions: 1) Desorb into the column for 4 minutes at <30°C; 2) hold at <30°C for one minute; 3) heat column to 100°C and hold for three minutes; and 4) program to 200°C at 8°/min.

Mass range scan	20-350
Integration time	12
Samples/AMU	1
Total Run	30 minutes

2) Polychlorinated biphenyls

See reference 4. Arochlors 1221, 1232, 1242, 1248, 1245, 1260 and 1016 were sought.

3) Bis(2-chloroethyl) ether and Bis-(2-chloroisopropyl) ether

See reference 5.

4) Vinyl chloride

Vinyl chloride was analyzed using a modified version of Bellar's and Lichtenberg's procedure.[6] Samples were collected in and purged from

70 ml septum sealed vials. This technique was employed to gain greater sensitivity from purging a larger sample and to eliminate losses to the headspace in the sample container. A microcoulometric detection system was employed. A chromasorb 101 column was operated isothermally at 100°C.

5) Organophosphate Pesticides

See reference 7. Phosdrin, Thimet, Diazinon, Disulfoton, Dimethoate, Ronnel, Merphos, Malathion, Methyl Parathion, Parathion, DEF, Ethion, Trithion, EPN and Guthion were sought.

b. General Organic Parameters

1) Non-volatile Total Organic Carbon

Non-volatile total organic carbon (NVTOC) is determined on an instrument made by Phase Separations Ltd., United Kingdom. Samples are acidified with nitric acid, purged with nitrogen gas for about 10 minutes to remove carbon dioxide, then pumped into the instrument at a constant rate of 0.6 ml/minute for about 10 minutes. After water and ammonia are removed the non-volatile organic carbon is thermally oxidized to carbon dioxide (CO_2) at 920°C with copper oxide as a catalyst, then reduced to methane (CH_4) at 450°C with nickel in a hydrogen atmosphere. The methane is analyzed with a flame ionization detector.

2) Ultraviolet Absorption

See reference 8.

3) Fluorescence

The Rapid Fluorometric Method (RFM) as described by Sylvia[9] and a fluorescence emission scan was performed. In this latter determination, the excitation and emission slit widths are 12 nm and 16 nm, respectively. The aqueous sample is excited at 310 nm and the fluorescence emission recorded between 370 nm and 580 nm.

c. Comprehensive Organic Analyses

In an attempt to determine as broad a range of organic compounds as possible in the samples collected from the First Series of the Comprehensive Locations (Table II), three different techniques of concentrating the organics were used. Because in all three cases the separation techniques involved the use of gas chromatography, only those organics in the water that can be volatilized and passed through the gas chromatograph were determined. This means that an undefined number of organic compounds that were originally in the sample, but non-volatile under the temperature of gas chromatographic conditions, were not determined. Techniques such as high pressure liquid chromatography and others would be needed to be applied to determine organic compounds with these properties.

Although three different concentrating techniques were used, they were not mutually exclusive. This means that certain organic compounds originally in the water would be determined by all three techniques. In general, however, one new technique[6] was designed to determine the lower boiling point (more volatile) organic compounds, that were not too soluble in water, while the other two techniques were used to determine organic compounds with higher boiling points. The concentration technique used to determine the lower boiling point organics begins by purging these organics from the liquid sample using helium. The higher boiling point organics were determined, in general, by liquid-liquid extraction with ethyl ether, and by adsorption onto granular activated carbon followed by desorption with chloroform. Details of all three procedures are contained in the three sub-sections that follow.

1) Organics Purged from Sample

Types of volatile organic analyses. Analysis for volatile organics is accomplished by the comparative analysis of three types of samples. These three types include: (a) head gas analysis in which some of the volatiles are allowed to escape into the head space above the water sample, and the gas is removed from the serum bottle and injected directly into a gas chromatography/mass spectrometry (GC/MS) system; (b) direct aqueous injection in which a small aliquot of the water sample is injected directly into a GC/MS system; and (c) active stripping of the organics in which a carrier gas removes the organics from the sample. The compounds then are adsorbed on a porous polymer medium, subsequently desorbed, separated by chromatographic techniques and analyzed with appropriate detectors. Although the method appears to emphasize the more volatile compounds, the ability to identify all "volatile" compounds is not within the scope of the method. Volatility is a chemical characteristic of a relative nature. The compounds amenable to the technique described below are those whose volatility is quite high, whose water solubility is quite low, and whose selective adsorptivity to the trapping medium is relatively high. Consequently, some volatile compounds may not be recovered by this technique.

Apparatus

Purging Apparatus. The method of Bellar and Lichtenberg[6] was applied to the purging of volatile organics from tap water samples. Two modifications were made to the original 5-ml purging device: a scale-up to 140 ml and to 500 ml. The 5-ml instrument was used for quantitation with the gas chromatograph and flame ionization detector. The 140-ml device was employed for quantitative assessment using the gas chromatograph with the mass spectrometer as detector in order to increase the sensitivity of detection. The 500-ml device was utilized for qualitative analysis only. Samples analyzed in the 500-ml instrument were dechlorinated prior to analysis. The actual design of the modified purgers is presented below.

140-ml Purger. This device was built by the Paxton Woods Glass Shop, Cincinnati, Ohio. The main difference between this device and that described by Bellar and Lichtenberg[6] is the capacity -- the original capacity was 5 ml; whereas, the modified version has a capacity of 140 ml.

The device has the appearance of a 140-ml gas washing bottle with:

1. A 29/42 ground-glass joint on the top.

2. A 20-mm medium fritted filter disc on the end of the gas tube to disperse the helium gas, an additional 5-mm (I.D.) sample port on the top of the male 29/42 joint.

3. A 6-mm (O.D.) by 9-mm (high) silicone rubber cylindrical injection septum fitted inside the injection port.

4. A 10-gauge and 762-mm long stainless steel hypodermic needle to penetrate the cylindrical rubber septum.

5. A stainless steel stopcock with male-female Luer-Lock fittings on the 10-gauge needle.

6. A water jacket surrounding the sample container for temperature control.

7. A 1/4-inch (O.D.) glass tubing on helium inlet and outlet ports.

8. A foam trap on the helium outlet trap.

The overall height of the device is approximately 27 cm.

500-ml Purger. The responsibility for the design and construction of this device is the same as for the 140-ml device. The 500-ml device is virtually identical to the 140-ml device, except for the higher sample capacity of 500 ml. In addition, the overall height of this device is approximately 44 cm. Specific modification includes a 3-mm (I.D.) by 6-mm (O.D.) by 42.5-cm (long) teflon tubing that was attached to the 10-gauge needle tip to prevent splashing during sample introduction.

Trapping Apparatus. The compounds stripped from the water were adsorbed onto a porous polymer, Tenax GC of 60/80 mesh. The size of the adsorbing column was adjusted to complement the size of the 500-ml stripping device. The trap for the 5-ml and 140-ml device is described by Bellar and Lichtenberg[6], and modifications of the trap for the 500-ml purger are as follows:

1. The stem is fabricated of 1/4-inch stainless steel tubing.

2. The length of the stem from 1/4-inch female swagelock fitting of the body assembly to the stem tip (trap inlet) is approximately 29 mm.

3. The stem assembly is made from Swagelock part number B-QC6-S-400 and body assembly from Swagelock part number B-QC4-B-400.

Desorption Apparatus. Desorption of organics from the three traps was accomplished by heat and the passage of helium gas as described by Bellar and Lichtenberg.[6] Three desorption units were utilized to accommodate the three trapping devices. The desorption unit used for quantitation with the flame ionization detector and the unit with the 5-ml trap are identical, respectively, to "desorber 1" and "desorber 2" described by Bellar and Lichtenberg.[6] The third desorption unit was employed with the 500-ml trap. This unit is composed of Swagelock part B-QC6-B-600 and has a total length of 26 cm.

Mass Spectrometry. When the mass spectrometer was employed as a detector, the following chromatographic conditions were established. The chromatographic instrument, the Finnigan 9000, was equipped with one of three columns: (a) ten-foot column packed with Chromosorb 101, (b) ten-foot column packed with Tenax GC, and (c) five-foot column packed with Chromosorb 101. All adsorbants were of 60/80 mesh.

Mass spectra were obtained on a Finnigan 1015D quadrupole instrument operating in the electron impact mode, and data were acquired and analyzed with the Systems Industries 150 computer system. Using graphic software, data (i.e., reconstructed gas chromatograms and mass spectra) were outputted on Tektronix 4010 crt data terminal. Operating parameters for the mass spectrometer and the data acquisition system are described below:

Mass Spectrometer. The mass spectrometer was operated in the following mode:

1. ionization potential = 70 eV
2. emission current = 500 μa
3. ion energy = 4 V
4. repeller potential = 6 V
5. lens potential = 100 V
6. analyzer temperature = 70 degrees C
7. continuous dynode electron multiplier detector = 2.0 KV

8. analyzer pressure = 5 x 10^{-6} Torr

9. output preamplifier = 10^{-7} amperes/V

10. mass range = 10 to 250 amu

11. daily calibrations according to manufacturer's specifications

Gas Chromatography. With the flame ionization detector, a Perkin-Elmer model 900 was utilized. Samples were analyzed on two different columns: (a) a six-foot column packed with Chromosorb 101 and (b) a six-foot column packed with Tenax GC. The former allows separation of compounds that elute early; whereas, the latter favors shorter retention of the compounds along with improved peak symmetry for later eluting compounds. Standards of chloroform, bromodichloromethane, dibromochloromethane, and of compounds identified from the mass spectrometric analyses and capable of yielding uncontaminated peaks with the flame ionization detector were analyzed daily.

Data Acquisition System

Data acquisition parameters were varied only as to the type of sample analyzed, and not from study city to study city. Four sets of data acquisition parameters were used: (a) one for qualitative head gas analyses and direct aqueous injection samples, (b) a second for head gas analyses of vinyl chloride, (c) a third for the 500-ml purged sample, and (d) another for all quantitative 140-ml purged samples.

1. For head gas analyses and direct aqueous injections:
    a. software program = IFSS
    b. mass range = 26-27, 29-31, 41-64, 72-78, 82-102, 112-133, 146-150 and 239 amu
    c. maximum repeat count = 4
    d. integration time = 17 msec
    e. repeat count before checking lower threshold = 4
    f. lower threshold = 4
    g. upper threshold = 1
2. For head gas analyses of vinyl chloride:
    a. software program = IFSS
    b. mass range = 27, 61-64, 83, 85 amu

c. maximum repeat count = 8

d. integration time = 68 msec

e. repeat count before checking lower threshold = 8

f. lower threshold = 4

g. upper threshold = 1

3. For the 500-ml purged samples:

   a. software program = IFSS

   b. mass range = 14-16, 19-27, 29-31, 33-240 amu

   c. maximum repeat count = 4

   d. integration time = 3 msec

   e. repeat count before checking lower threshold = 4

   f. lower threshold = 4

   g. upper threshold = 4

4. For quantitation using 140-ml purged samples:

   a. software program = IFSS

   b. mass range = 26-27, 29-31, 41-102, 112-133, 146-150, 166-177, 239 amu

   c. maximum repeat count = 4

   d. integration time = 4 msec

   e. repeat count before checking lower threshold = 4

   f. lower threshold = 4

   g. upper threshold = 1

Reagents. Water low in organic carbon was prepared by purging Millipore Super Q pre-distilled water with helium at a rate of 60 ml per minute for 38 hours at 95 degrees C. (Organic-free water was impossible to obtain.) This water was used for blanks and for the preparation of standards. Potassium ferrocyanide was used to eliminate chlorine and chloramines in 500-ml samples to be purged at 95 degrees C.

Procedure

Purging. Blanks, 140-ml samples, and 500-ml samples were transferred in the following manner:

a. inversion of serum bottle,

b. penetration of the septum with a 10-gauge hypodermic needle connected to the introduction port of the appropriate purging device,

c. penetration of the same septum with a second hypodermic needle (20-gauge and 6 inches in length) connected to a helium supply,

d. application of gas (helium at a flow rate of 20 ml/min) pressure to force the sample out of the bottle.

Organic standards used in the 5-ml and 140-ml purging devices were prepared by a procedure previously described.[6]

Additional information about the procedures for purging, adsorption, desorption and chromatographic and spectral analyses will be presented in the December 1975 report.

2) Organics Extracted from Sample with Solvent

After measuring the pH of the gallon sample, three liters were transferred to a six-liter separatory funnel. Fifty milliliters of ethyl ether were added, and the mixture was shaken for one minute. The sample was then extracted three times with 75 ml portions of methylene chloride, and the extracts were combined in a 300-ml erlenmeyer flask. The purpose of the ethyl ether is to improve the extraction efficiency of the more polar compounds like phenols and acids.

The combined extract was poured through two inches of anhydrous sodium sulfate in a 19-mm I.D. glass column. As an added precaution, the anhydrous sodium sulfate was prerinsed with 100-ml methylene chloride to remove any impurities. The dried extract was collected in a 500-ml Kuderna-Danish (K-D) flask fitted with a 10-ml ampule graduated in 0.1 ml increments.

After the combined extract had filtered through the sodium sulfate, the sodium sulfate was rinsed with 50 ml of acetone. This was done for two reasons: to rinse any residual sample components from the sodium sulfate, and to introduce a nonchlorinated solvent into the sample for GC/MS injection.

The pH of the water layer was then adjusted to 2.0 using concentrated HCl and the above steps repeated. In the first step, it was not necessary to add the ethyl ether a second time.

When the second extraction was completed, the pH of the water layer was adjusted to 12.0 using a saturated NaOH solution. Again, the extraction and drying steps were repeated, ignoring the addition of ethyl ether. The three sample extracts were now contained in three K-D flasks: the neutral compounds extracted from a solution of approximately pH 7, the acid compounds extracted from a solution of pH 2, and the basic compounds extracted from a solution of pH 12. The reagent blank was in a separate K-D flask.

A Snyder column was fitted to each K-D flask, and the extracts were concentrated on a steam bath to approximately 5 ml. After concentration, the methylene chloride (BP = 39.8°C) was completely removed and the sample was contained in acetone (BP = 56.1°C). The acetone was used because one or two microliters of methylene chloride will cause an excessive increase in the pressure in the mass spectrometer and automatically shut down the system, whereas up to 8 microliters of acetone will not cause this undesirable situation. The extracts were further concentrated in the ampule to 100 µl in a warm water bath under stream of clean, dry nitrogen with repeated rinsing of the inside of the ampule. Five microliter injections were made into the GC/MS.

The GC column used in this study is 6 ft by 2 mm I.D., packed with Supelcoport (80/100 mesh) coated with 1.5% OV-17 and 1.95% QF-1. The initial column temperature was 60°C, which was held for 1.5 minutes, then the temperature was programmed at 3° per minute to a final temperature of 220°C which was held for 15 minutes. The total run time was approximately 35 minutes.

The sample run was set up as follows:

System 150 is on select mode: Cont

Calibrate?: No

Title: Enter appropriate title

Calibration file name: Cal

File name: Enter appropriate file name

Mass range: 33-450

Integration time: 8

Samples/AMU: 1

Threshold:

RT GC Atten: 7

Fast scan opt?:

MS range setting?: H

Max run time: 35

Delay between scans (sec)?:

3) Organics Adsorbed on Activated Carbon from Sample

CAM Carbon Processing. On removal from the sampling sites, the CAM carbon cylinders were drained of excess water, sealed and shipped by commercial air carrier to the processing laboratory. The columns were stored at 4°C until carbon processing could be initiated.

Columns were opened in a special activated carbon handling room designed to minimize the potential for contamination. The activated carbon was transferred to Pyrex glass dishes and dried at 35-38°C for 48 hours under a gentle flow of clean air in a mechanical convection oven. The oven air inlet was equipped with an activated carbon filter to prevent atmospheric contamination.

The dried activated carbon was transferred to 220-ml Soxhlet extractors and extracted for 48 hours with chloroform. The chloroform extracts were filtered through solvent-extracted glass fiber filters to remove activated carbon fines and then vacuum concentrated at temperatures not exceeding 27°C in rotary evaporators to final volumes of 30-60 ml. The concentrated extracts were transferred quantitatively to 10-ml ampules, several ampules being required to accommodate each extract. The ampules were purged with dry, clean nitrogen and sealed while the contents were held at -50°C in a cold bath. The filled ampules were maintained under refrigeration (4°C) until shipment to the analytical laboratory by air mail.

Gas Chromatography - Mass Spectrometry. Gas chromatography was performed using a Varian 1400GC with a flame ionization detector. Carbon chloroform extracts (CCE's) were received in sealed glass ampules from the R. S. Kerr Environmental Research Laboratory. After each CCE volume was measured it was concentrated in a Kuderna-Danish apparatus to about 8 ml. Concentration to a final volume of 6 ml was achieved by blowing a gentle stream of nitrogen over the surface of the extract at room temperature. Since 6,000 liters of water were passed through each filter, the organics in each 6-ml extract are 1 million times more concentrated than in the original water sample. However, the percent adsorption on carbon, percent desorption into the solvent, and percent loss on concentration of the solvent are unknown and vary with each individual compound. Therefore, the quantitation of each compound is only approximate and the quantity of each chemical reported can be considered as its minimum concentration.

Concentrated extracts were analyzed with a computerized combined gas chromatograph-mass spectrometer (GC-MS) system. A Finnigan 1015 quadrupole mass spectrometer was operated in the electron impact mode and data was acquired using a System Industries 150 computer interface. A Varian 1400 gas chromatograph was interfaced directly to the mass spectrometer with a 9-inch stainless steel capillary tube. The gas chromatograph contained a 30-meter by 0.4-mm I.D. glass capillary column (No. 646) coated with Supelco SP-2100 at the Southeast Environmental Research Laboratory.

Optimized gas chromatographic conditions included multiple temperature and carrier gas (helium) flow programming. Injection of 0.4 μl of each sample was made with the GC oven door open, the column at room temperature (about 30°C), and the MS pressure at 1.5 x 10^{-5} torr. The GC oven door was closed 5 minutes after injection and the temperature slowly increased to about 50° over the next 6 minutes. At 11 minutes after injection the oven temperature controller was set at 60°. Two minutes later temperature programming at 2°/min was started. Twenty-three minutes after injection (80°C) the temperature program rate was increased to 6°/min and carrier gas flow was increased to produce a MS pressure of 2.8 x 10^{-5} torr (previously determined to correspond to a helium flow of 2 cc/min at room temperature). Thirty-three minutes after injection (140°C) the temperature program rate was increased to 10°/min. The final temperature of 250°C was maintained for 20 minutes.

Computer-controlled collection of mass spectral data was begun immediately after sample injection. To prevent filament damage as solvent entered the MS, the ionization current was shut off 2.5 minutes after injection and turned on again 3.5 minutes after injection. Electron energy was maintained at 70 eV and filament current at 400 μa. A mass spectrum from m/e 41 to 350 was acquired approximately every 2.5 seconds by the PDP-8/e computer.

At the end of data acquisition a computer-reconstructed gas chromatogram was plotted. Sample spectra were then chosen and plotted after appropriate background spectra were subtracted. Spectral matching was performed using the EPA computerized Mass Spectral Search System at the National Institutes of Health in Washington, D.C. Tentative identifications of compounds were based on these spectral matches and on interpretation of the mass spectra.

To confirm these identifications, mass spectra and gas chromatographic retention times of mixtures of standards (when available) were compared with those of sample components. The retention times of these components were calculated relative to camphor because it was present in the CCE blank and therefore in all samples. Camphor also served as the internal standard used for all the standard mixtures.

Concentrations were calculated with a computer program that compared the total ion current (TIC) summation of sample component mass spectra with the TIC summation of a known amount of that compound in the standard solution. When a standard was not available, a standard compound of similar molecular structure was used to estimate the quantity of the tentatively-identified sample component.

Processing Blanks. The foregoing discussion of preparation and analytical methods has been concerned with the processing of actual samples. However, to assure that components identified were actually derived from the original samples and were not artifacts, contaminants, or inherent components deriving from the sampling method itself, the sampling media, commercial solvents, or the sample preparations, it was necessary to process blank samples taken through all stages of the operations in parallel with the actual samples, including washing the sampling activated carbon with activated carbon treated water to remove any water soluble materials.

As a consequence of this processing of blanks through the analytical stage, no components could be accepted as deriving from the finished water samples unless these components were not present at a significant level in the blanks relative to the samples.

d. Constituents in Drinking Water Regulations

1) Inorganics

Analytical methods to determine compliance with the requirements of the regulations shall be those specified in the current (13th) Edition of Standard Methods for the Examination of Water and Wastewater (SMEWW), published by the American Public Health Association,[10] and/or Methods for Chemical Analysis of Water and Wastewater (MCAWW), U.S. Environmental Protection Agency, 1974,[11] except for the following which are either not in the current editions, or are undergoing extensive revision.

Arsenic and Selenium. The atomic absorption spectrophotometer method is preferable to the wet chemical procedures in the present edition of SMEWW as these will conserve time and effort in analysis and produce improved sensitivity, see reference 12. This procedure will also appear in the 14th Edition of SMEWW and the 1974 Edition of MCAWW.

Cyanide. See reference 13.

Mercury. See reference 14. This procedure will appear in the 14th Edition of SMEWW and is the same as that appearing in MCAWW.[11]

2) Organics - Carbon Adsorbable (CCE-m)

See reference 1.

3) Pesticides (chlorinated hydrocarbons), 2,4-D and Silvex

See references 15 and 16. Table 5 lists all the chlorinated hydrocarbons sought.

TABLE 5

Organochlorine Pesticides
α BHC
PCNB
Lindane
Dichloran
Heptachlor
Aldrin
Heptachlor Epoxide
Endosulfan
p,p' DDE
Dieldrin
Captan
Endrin
DDT
p,p' DDD
Mirex
Methoxychlor
Tech. Chlordane
Toxaphene

4. Quality Control

Accuracy

To test the accuracy of the method as used by Water Supply Research Laboratory during the survey, a pair of "unknown" standard mixtures was prepared by another EPA laboratory in the following manner:

Two different stock solutions each containing all of the compounds of interest were prepared by injecting a known volume of each material into a volumetric flask containing 90 ml of methyl alcohol. After all of the compounds were injected into the flask the mixture was diluted to volume (100.0 ml) and mixed by inverting. Two hundred microliters of the stock solution was then dosed into 1.0 liter of super-Q water and mixed by inverting two times. One-half of the dosed water was then transferred into a 500 ml separatory funnel. Several 60-ml vials were then filled with the mixture and promptly sealed with Teflon septums. The samples were stored at 4°C until delivery to Water Supply Research Laboratory. The blank (Sample D-4) contained only super-Q water. The calculated concentrations of the dosed mixtures, D-2 and D-3, are listed with the analytical results in Table 6.

Analysis by the respective laboratories was exactly as described in the Section C(3)(a)(1), for the determination of the six halogenated organic compounds: chloroform, bromodichloromethane, dibromochloromethane, bromoform, carbon tetrachloride, and 1,2-dichloromethane.

Precision

To test variability of results during a typical day of analysis, two series of 5 replicate samples were prepared as ten discrete samples in the same manner as standards were prepared throughout the survey. One series was at low concentrations and the other at high concentrations. All of the samples were analyzed exactly as described in Section C (3)(a)(1) for the determination of the six halogenated organic compounds, chloroform, bromodichloromethane, dibromochloromethane, bromoform, carbon tetrachloride, 1,2-dichloroethane. Spiked concentrations and relative standard deviations (σ/XAV) are listed in Table 7.

D. RESULTS

At this time (April 1975), all of the results of the National Organics Reconnaissance Survey are not complete. Work is continuing on several facets of the Survey. For this interim report, all of the results available at the present time will be presented, summarized, and discussed. The December 1975 report will contain all of the data.

TABLE 6

DETERMINATION OF ACCURACY

Concentration (μg/l)

Sample	Chloroform	1,2-Dichloroethane	Carbon tetrachloride	Bromodichloromethane	Dibromochloromethane	Bromoform
D-2 (True Value)	74.6	10.1	9.5	39.6	23.8	40.4
D-2a (Prim. Lab.)	63	9	9	39	23	40
D-2b (Prim. Lab.)	65	10	8	40	23	38
D-2 (Conf. Lab.)						
D-2 (Conf. Lab.)						
D-3 (True Value)	59.6	5.0	6.4	23.8	19.0	23.2
D-3a (Prim. Lab.)	46	6	5	22	14	18
D-3b (Prim. Lab.)	46	5	6	23	18	24
D-3 (Conf. Lab.)						
D-3 (Conf. Lab.)						
D-4b (Blank-Prim. Lab.)	0.2	1	NF	NF	NF	NF

TABLE 7

SPIKED CONCENTRATIONS AND RELATIVE STANDARD DEVIATIONS

Compound	Conc. (μg/1)	Rel. σ(%)	Conc. (μg/1)	Rel. σ(%)
Chloroform	2.	6	18	7
1,2-Dichloroethane	1.	5	*	*
Carbon Tetrachloride	2.	14	*	*
Bromodichloromethane	2.	5	20	7
Dibromochloromethane	2.	10	30	13
Bromoform	4.	20	30	12

*Not determined at high concentrations.

1. Source and Treatment Information

At the time of the preparation of this report, engineering data were available on the water supplies of 59 locations. Table 8 shows the percentages of these 59 locations that used the different categories of sources studied in this investigation. Table 8 also shows the treatment practices of these 59 locations. When all the data are in, a study population from 25-30 million is expected.

Because a major objective of this study was to determine the effect of disinfection practices on the formation of the 4 trihalomethanes, Table 9 shows the distribution of the prechlorination dosages used at the 42 locations where prechlorination was practiced. In 82% of these locations the prechlorination dose was between 1 and 6 mg/l. Table 10 shows the distribution of the concentration of chlorine residual, both free and combined. In general, rather low residuals were present in the finished waters studied, and at 20% of the locations there was less than 0.4 mg/l of either free or combined residual.

2. 80 Location Study

a. Raw Water Data

The data summarized in Table 11 shows that the six selected compounds measured in the raw water at the 80 locations were mostly absent or present in very low concentrations. One location was receiving water prechlorinated by others and this water did contain some chloroform, bromodichloromethane and dibromochloromethane. Non-volatile total organic carbon determinations were made on each sample but were not reported as they were considered unreliable because of the presence of suspended solids in the samples. This was also true of the ultraviolet absorption and fluorescence data.

TABLE 8

SUMMARY OF ENGINEERING DATA

(All Percentages are of 59 Locations)

Source	
Ground	24%
Lake or Reservoir	37%
River	39%
Mixed	0%
Treatment	
Prechlorination	71%
Filtration	73%
Polyelectrolyte	20%
Powdered Activated Carbon	22%
Granular Activated Carbon	9%
Softening	
Precipitative	17%
Zeolite	3%
Taste and Odor Control Practiced	37%

Note: One location was pre-ozonated and another used ozonation as the only treatment.

TABLE 9

PRECHLORINATION DOSAGES

(All Percentages of 42 Locations)

0-1 mg/l	10%
1-2 mg/l	29%
2-3 mg/l	8%
3-4 mg/l	17%
4-5 mg/l	14%
5-6 mg/l	14%
6-7 mg/l	2%
7-8 mg/l	0%
8-9 mg/l	2%
>10 mg/l	2%
Unknown	2%

b. Finished Water Data

1) Organics

Table 12 summarizes all of the data on finished water quality from the 80 locations. The ultraviolet absorption and fluorescence data were not presented at this time as their significance, if any, are not currently known. The range of each measurement is noted at the end of the Table.

To show the central tendency of the data, Table 13 presents the frequency distribution of the concentrations of six selected organic compounds measured in all 80 locations as well as the concentration of finished water non-volatile total organic carbon. Each of these seven parameters is not evenly distributed over the range but is biased toward the low concentration end of the range. Therefore, high concentrations of these parameters were a somewhat unusual occurrence in this study.

2) Inorganics

Table 14 contains the concentrations of the inorganic substances in the Interim Primary Drinking Water Regulations. Very few locations exceeded the limits.

3. Confirmation Samples

a. Quantitative

The data presented in Tables 15a and 15b show good quantitative confirmation of the routine analysis of the six selected compounds in the

TABLE 10

CHLORINE RESIDUAL

(All Percentages of 56 Locations)

Combined Residual - mg/l	
0-0.4	63%
0.4-0.8	20%
0.8-1.2	4%
1.2-1.6	2%
1.6-2.0	5%
2.0-2.4	2%
2.4-2.8	4%
Free Residual - mg/l	
0-0.4	43%
0.4-0.8	20%
0.8-1.2	5%
1.2-1.6	17%
1.6-2.0	4%
2.0-2.4	7%
2.4-2.8	4%
Free and Combined Residual	
Each 0-0.4 mg/l	20%

TABLE 11

RAW WATER DATA

	Chloroform µg/1	Bromo-dichloro-methane µg/1	Dibromo chloro methane µg/1	Bromo form µg/1	1,2-Dichloro-ethane µg/1	Carbon Tetra-chloride µg/1	Non-Volatile Tota Organic Carbon mg/1
1. Lawrence, Massachusetts ------------	<0.1	<0.2	NF	NF	NF	NF	3.7
2. Waterbury, Connecticut -------------	NF	NF	NF	NF	NF	NF	2.2
3. Boston, Mass. (Metropolitan Dist. Comn.) ---------------------	NF	NF	NF	NF	NF	NF	2.1
4. Newport, Rhode Island (Plant #1) ---	NF	NF	NF	NF	NF	NF	4.6
5. New York, New York -----------------	NF	NF	NF	NF	NF	NF	3.0
6. San Juan, P.R. (Sergio Cuevas Plant) --------------------	<0.2	NF	NF	NF	NF	NF	2.0
7. Little Falls, N.J., Passaic Valley Water Comn. --------------	0.3	NF	NF	NF	<0.2	<2	3.6
8. Toms River, New Jersey ------------	0.4	NF	NF	NF	NF	NF	<0.05
9. Buffalo, New York -----------------	NF	NF	NF	NF	NF	NF	2.6
10. Rhinebeck, New York ---------------	0.3	NF	NF	NF	NF	NF	3.5
11. Philadelphia, Pa. (Torresdale Plant) --------------	0.2	NF	NF	NF	3	NF	2.6
12. Stanton, Delaware, Wilmington Suburban --------------	0.3	<0.4	NF	NF	NF	NF	2.8
13. Newark, Delaware, Artesian Water Company -------------------	0.2	NF	NF	NF	NF	NF	3.6
14. Washington, D.C., Wash. Aqueduct (Dalecarlia Plant -------	<0.2	NF	NF	NF	NF	NF	1.8
15. Baltimore, Maryland ---------------	NF	NF	NF	NF	NF	NF	1.8
16. South Pittsburgh, Pa., West. Penn. Water Co., (Hays Mine Plant) ---------------------	0.3	NF	NF	NF	NF	NF	0.9
17. Strasburg, Pennsylvania -----------	NF	NF	NF	NF	NF	NF	0.2
18. Annnandale, Va., Fairfax County Water Authority (New Lorton Plant) ---------------	<0.2	<0.4	NF	NF	NF	NF	4.7
19. Hopewell, Virginia ----------------							(Postponec

Table 11 (Continued)

	Chloroform µg/l	Bromo-dichloro-methane µg/l	Dibromo chloro methane µg/l	Bromo form µg/l	1,2-Dichloro-ethane µg/l	Carbon Tetra-chloride µg/l	Non-Volatile Total* Organic Carbon mg/l
20. Huntington, West Virginia	1	NF	NF	NF	< <0.3	4	2.2
21. Wheeling, West Virginia	0.2	NF	NF	NF	<0.3	NF	3.2
22. Miami, Florida (Preston Plant)	NF	NF	NF	NF	<0.2	<2	9.8
23. Jacksonville, Florida	NF	NF	NF	NF	NF	NF	2.4
24. Atlanta, Georgia (Chattahoochee Plant)	<0.2	NF	NF	NF	<0.3	NF	1.3
25. Owensboro, Kentucky	NF	NF	NF	NF	NF	NF	1.7
26. Greenville, Mississippi	0.3	NF	NF	NF	NF	NF	3.3
27. Chattanooga, Tenn., Tenn. American Water Co.	0.9	NF	NF	NF	NF	NF	1.1
28. Memphis, Tennessee	<0.2	NF	NF	NF	NF	NF	0.2
29. Nashville, Tennessee	<0.1	NF	NF	NF	NF	NF	1.2
30. Charleston, S.C. (Stoney Plant)	<0.2	NF	NF	NF	NF	NF	11.4
31. Cincinnati, Ohio	0.5	NF	NF	NF	NF	2	2.3
32. Chicago, Illinois (South Plant)	<0.2/0.4	NF/0.5	NF/NF	NF/NF	NF/NF	NF/NF	1.9/1.7
33. Clinton, Illinois	<0.2	NF	NF	NF	NF	NF	7.7
34. Indianapolis, Indiana (White River Plant)	0.1	NF	NF	NF	<0.3	NF	5.1
35. Whiting, Indiana	16	11	3	NF	NF	NF	2.0
36. Detroit, Michigan (Park Plant)	<0.2	NF	NF	NF	NF	NF	2.6
37a. Mt. Clemens, Michigan	NF	NF	NF	NF	NF	NF	2.0
37b. Mt. Clemens, Michigan	0.9	NF	NF	NF	<0.2	NF	6.7 (After replacement c granular ac carbon)
38. St. Paul, Minnesota	<0.2	NF	NF	NF	NF	NF	7.9
39. Cleveland, Ohio (Division Plant)	NF	NF	NF	NF	NF	NF	2.2
40. Columbus, Ohio (Dublin Plant)	0.1	NF	NF	NF	NF	NF	6.8
41. Dayton, Ohio (Ottawa Plant)	NF	NF	NF	NF	NF	NF	0.9
42. Indian Hill, Ohio	<0.2	NF	NF	NF	NF	NF	0.8
43. Piqua, Ohio	NF	NF	NF	NF	NF	NF	6.0

Table 11 (Continued)

	Chloroform µg/1	Bromo-dichloro-methane µg/1	Dibromo chloro methane µg/1	Bromo form µg/1	1,2-Dichloro-ethane µg/1	Carbon Tetra-chloride µg/1	Non-Volatile Total* Organic Carbon mg/1
44. Youngstown, Ohio (Mahoning Valley San. Dist.)	NF	NF	NF	NF	NF	NF	4.7
45. Milwaukee, Wisconsin (Howard Ave. Plant)	<0.2	NF	NF	NF	NF	NF	2.4
46. Oshkosh, Wisconsin	NF	NF	NF	NF	NF	NF	4.5
47. Houma, La., Terrebonne Parish Water Works #1	NF	NF	NF	NF	NF	NF	5.4
48. Camden, Arkansas	NF	NF	NF	NF	NF	NF	3.1
49. Logansport, Louisiana	0.7	NF	NF	NF	NF	NF	5.3
50. Albuquerque, New Mexico	NF	NF	NF	NF	NF	NF	<0.05
51. Oklahoma City, Okla. (Hefner Plant)	NF	NF	NF	NF	NF	NF	3.6
52. Brownsville, Texas (Plant #2)	NF	NF	NF	NF	NF	NF	4.7
53. Dallas, Texas (Bachman Plant)	<0.1	NF	NF	NF	NF	NF	3.4
54. San Antonio, Texas	NF	NF	NF	NF	NF	NF	0.5
55a. Ottumwa, Iowa	<0.2	NF	NF	NF	NF	NF	4.1 (2/17/75 sample)
55b. Ottumwa, Iowa	NF	NF	NF	NF	NF	NF	4.9 (4/7/75 sample)
56. Clarinda, Iowa	<0.2	NF	NF	NF	NF	NF	3.5
57. Davenport, Iowa	0.4	NF	NF	NF	NF	NF	6.5
58. Topeka, Kansas	0.4	0.8	NF	NF	NF	NF	3.4
59. Cape Girardeau, Mo., Mo. Utilities Co.	0.2	NF	NF	NF	0.2	NF	4.5
60. Kansas City, Missouri	NF	NF	NF	NF	NF	NF	3.4
61. St. Louis, Missouri, St. Louis County Wat. Co., (Central Plant)	NF	NF	NF	NF	0.3	NF	3.4
62. Lincoln, Nebraska	NF	NF	NF	NF	NF	NF	1.4
63. Grand Forks, North Dakota	NF	NF	NF	NF	NF	NF	9.2

Table 11 (Continued)

	Chloroform µg/l	Bromo-dichloro-methane µg/l	Dibromo chloro methane µg/l	Bromo form µg/l	1,2-Dichloro-ethane µg/l	Carbon Tetra-chloride µg/l	Non-Volatile Total* Organic Carbon mg/l
64. Denver, Colorado (North Side Marston Plant)	<0.2	NF	NF	NF	NF	NF	2.0
65. Pueblo, Colorado (Gardner Plant)	<0.2	NF	NF	NF	NF	NF	1.8
66. Huron, South Dakota	NF	NF	NF	NF	NF	NF	19.2
67. Salt Lake City, Utah (Parleys Plant)	0.2	NF	NF	NF	0.4	NF	1.2
68. Tuscon, Arizona (Plant #1)	<0.1	NF	NF	NF	NF	NF	<0.05
69. Phoenix, Arizona (Verde Plant)	<0.2	NF	NF	NF	NF	NF	1.0
70. Coalinga, Calif. (Coalinga Mun. Water Plant)	<0.2	NF	NF	NF	NF	NF	3.7
71. Concord, Cal., Contra Costa Cnty. Wat. Dist., (Bollman Plant)	0.3	0.3	NF	NF	NF	NF	3.4
72. Dos Palos, California	NF	NF	NF	NF	NF	NF	4.4
73. Los Angeles, California (Owen's Aqueduct)	<0.1	NF	NF	NF	NF	NF	1.2
74. San Diego, California (Miramar Plant)	NF	NF	NF	NF	NF	NF	2.9
75. San Francisco, Calif. (San Andreas Plant)	NF	NF	NF	NF	NF	NF	1.3
76. Seattle, Washington (Cedar River)	<0.2	NF	NF	NF	NF	NF	0.9 (End of Dis System)
77. Douglas, Alaska	NF	NF	NF	NF	NF	NF	3.4
78. Idaho Falls, Idaho	<0.2	NF	NF	NF	NF	NF	0.5
79. Corvallis, Oregon (Taylor Plant)	NF	NF	NF	NF	NF	NF	1.0
80. Ilwaco, Washington	0.1	NF	NF	NF	NF	NF	7.5
Range	<0.1 - 0.9	<0.2-0.8	NF	NF	<0.2-3	<2-4	<0.05-19.2

NF - None Found

* - May be low because of incomplete combustion of particulates in raw water.

TABLE 11 (Cont'd.)

SUMMARY OF RAW WATER ANALYSIS

	Number of Locations	Range, μg/l
Nothing found	30	-
Chloroform	45	<0.1 - 0.9
Bromodichloromethane	6	<0.2 - <0.8
Dibromochloromethane	0	-
Bromoform	0	-
1,2-Dichloroethane	11	<0.2 - 3
Carbon Tetrachloride	4	<2 - 4

Table 12

FINISHED WATER DATA

	Chloroform µg/l	Bromo-dichloro-methane µg/l	Dibromo chloro methane µg/l	Bromo form µg/l	1,2-Dichloro-ethane µg/l	Carbon Tetra-chloride µg/l	Non-Volatile Total Organic Carbon mg/l
1. Lawrence, Massachusetts	91	9	0.6	NF	NF	NF	1.6
2. Waterbury, Connecticut	93	10	0.6	<1	<0.2	<2	2.9
3. Boston, Mass. (Metropolitan Dist. Comn.)	4	0.8	NF	NF	NF	NF	2.0
4. Newport, Rhode Island (Plant #1)	103	42	13	1	NF	NF	4.1
5. New York, New York	22	7	0.9	NF	NF	NF	2.5
6. San Juan, P.R. (Sergio Cuevas Plant)	47	29	16	2	NF	NF	2.0
7. Little Falls, N.J., Passaic Valley Valley Water Comn.	59	16	2	NF	<0.2	<2	1.9
8. Toms River, New Jersey	0.6	<0.8	3	NF	NF	NF	<0.05
9. Buffalo, New York	10	10	4	NF	<0.2	NF	1.7
10. Rhinebeck, New York	49	11	1	NF	2	NF	1.6
11. Philadelphia, Pa. (Torresdale Plant)	86	9	5	NF	6	NF	1.7
12. Stanton, Delaware, Wilmington Suburban	23	11	3	NF	<0.4	<2	1.8
13. Newark, Delaware, Artesian Water Company	0.5	0.5	1	<1	<0.2	NF	0.2
14. Washington, D.C., Wash. Aqueduct (Dalecarlia Plant)	41	8	2	NF	<0.3	NF	1.2
15. Baltimore, Maryland	32	11	2	NF	NF	NF	1.2
16. South Pittsburgh, Pa., West. Penn. Water Co., (Hays Mine Plant)	8	2	0.4	NF	NF	NF	0.8
17. Strasburg, Pennsylvania	<0.1	NF	NF	NF	NF	NF	0.05
18. Annandale, Va., Fairfax County Water Authority (New Lorton Plant)	67	6	<0.6	NF	NF	NF	2.7
19. Hopewell, Virginia							(Postponed)

Table 12 (Continued)

	Chloroform µg/l	Bromo-dichloro-methane µg/l	Dibromo chloro methane µg/l	Bromo form µg/l	1,2-Dichloro-ethane µg/l	Carbon Tetra-chloride µg/l	Non-Volatile Total Organic Carbon mg/l
20. Huntington, West Virginia	23	16	5	NF	<0.4	3	1.0
21. Wheeling, West Virginia	72	28	17	NF	<0.4	NF	1.8
22. Miami, Florida (Preston Plant)	311	78	35	3	<.2	NF	5.4
23. Jacksonville, Florida	9	4	2	NF	NF	NF	2.3
24. Atlanta, Georgia (Chattahoochee Plant)	36	10	2	NF	NF	NF	0.9
25. Owensboro, Kentucky	13	20	17	3	NF	NF	2.0
26. Greenville, Mississippi	17	6	3	<1	<0.2	NF	4.0
27. Chattanooga, Tenn., Tenn. American Water Co.	30	9	0.7	NF	<0.4	NF	0.6
28. Memphis, Tennessee	0.9	2	1	NF	NF	NF	0.2
29. Nashville, Tennessee	16	5	<0.4	NF	NF	NF	0.8
30. Charleston, S.C. (Stoney Plant)	195	9	0.8	0.8	NF	NF	4.1
31. Cincinnati, Ohio	45	13	4	NF	<0.4	<2	1.1
32. Chicago, Illinois (South Plant)	15	10	4	NF	<0.4	NF	1.5
33. Clinton, Illinois	4	0.5	NF	NF	NF	NF	6.7
34. Indianapolis, Indiana (White River Plant)	31	8	<2	NF	NF	2	2.6
35. Whiting, Indiana	0.5	0.3	NF	NF	NF	NF	1.5
36. Detroit, Michigan (Park Plant)	12	9	3	NF	0.4	NF	1.2
37a. Mt. Clemens, Michigan	11	6	2	NF	<0.4	NF	1.4
37b. Mt. Clemens, Michigan	6	3	2	NF	NF	NF	1.4 (After re-placement of granular act. carbon)
38. St. Paul, Minnesota	44	7	<2	NF	NF	NF	4.4
39. Cleveland, Ohio (Division Plant)	18	9	4	NF	NF	NF	1.8
40. Columbus, Ohio (Dublin Plant)	134	8	<0.4	NF	NF	NF	2.3
41. Dayton, Ohio (Ottawa Plant)	8	8	11	4	<0.2	<2	0.7
42. Indian Hill, Ohio	5	7	11	NF	NF	NF	0.9
43. Piqua, Ohio	131	13	3	NF	<0.2	NF	4.2
44. Youngstown, Ohio (Mahoning Valley San. Dist.	80	5	<1	NF	NF	NF	3.1

Table 12 (Continued)

	Chloroform µg/l	Bromo-dichloro-methane µg/l	Dibromo chloro methane µg/l	Bromo form µg/l	1,2-Dichloro-ethane µg/l	Carbon Tetra-chloride µg/l	Non-Volatile Total Organic Carbon mg/l
45. Milwaukee, Wisconsin (Howard Ave. Plant	9	7	3	NF	<0.2	NF	1.7
46. Oshkosh, Wisconsin	26	4	<0.4	NF	<0.2	NF	3.3
47. Houma, La., Terrebonne Parish Water Works #1	134	32	8	<1	0.2	NF	3.2
48. Camden, Arkansas	40	19	7	NF	NF	NF	1.5
49. Logansport, Louisiana	28	39	24	3	NF	NF	3.5
50. Albuquerque, New Mexico	0.4	1	2	3	NF	NF	<0.05
51. Oklahoma City, Okla. (Hefner Plant)	44	28	20	6	<0.4	<2	2.8
52. Brownsville, Texas (Plant #2)	12	37	100	92	NF	NF	3.1
53. Dallas, Texas (Bachman Plant)	18	4	<2	NF	NF	NF	2.9
54. San Antonio, Texas	0.2	0.9	3	3	NF	NF	0.5
55a. Ottumwa, Iowa	0.8	NF	NF	NF	NF	NF	2.3 (2/17/75 sample)
55b. Ottumwa, Iowa	1	NF	NF	NF	NF	NF	2.4 (4/7/75 sample)
56. Clarinda, Iowa	48	19	4	NF	NF	NF	3.0
57. Davenport, Iowa	88	8	<0.6	NF	<0.4	NF	4.4
58. Topeka, Kansas	88	38	19	5	NF	3	2.2
59. Cape Girardeau, Mo., Mo. Utilities Co.	116	21	2	NF	0.3	2	3.6
60. Kansas City, Missouri	24	8	2	NF	NF	NF	1.9
61. St. Louis, Missouri, St. Louis Wat. Co., (Central Plant)	55	13	3	<1	0.4	NF	2.6
62. Lincoln, Nebraska	4	6	4	<2	NF	NF	1.4
63. Grand Forks, North Dakota	3	1	NF	NF	NF	NF	5.2
64. Denver, Colorado (North Side Marston Plant)	14	10	3	NF	NF	NF	1.7
65. Pueblo, Colorado (Gardner Plant)	2	2	<2	NF	NF	NF	1.6

Table 12 (Continued)

	Chloroform µg/l	Bromo-dichloro-methane µg/l	Dibromo chloro methane µg/l	Bromo form µg/l	1,2-Dichloro-ethane µg/l	Carbon Tetra-chloride µg/l	Non-Volatile Total Organic Carbon mg/l
66. Huron, South Dakota	309	116	49	8	NF	NF	12.2
67. Salt Lake City, Utah (Parleys Plant)	20	14	8	NF	NF	NF	0.9
68. Tuscon, Arizona (Plant #1)	<0.2	<0.8	2	13	NF	NF	<0.05
69. Phoenix, Arizona (Verde Plant)	9	15	17	<4	NF	NF	1.0
70. Coalinga, Calif. (Coalinga Mun. Water Plant)	16	17	15	2	NF	NF	2.4
71. Concord, Cal., Contra Costa Cnty. Wat. Dist., (Bollman Plant)	31	18	6	<1	NF	NF	1.9
72. Dos Palos, California	61	53	34	7	NF	NF	2.9
73. Los Angeles, California (Owen's Aqueduct)	32	6	3	NF	NF	NF	1.3
74. San Diego, California (Miramar Plant)	52	30	19	3	NF	NF	2.8
75. San Francisco, Calif. (San Andreas Plant)	41	15	4	<0.8	NF	NF	1.6
76. Seattle, Washington (Cedar River)	15	0.9	NF	NF	NF	NF	0.9 (End of Dst. System)
77. Douglas, Alaska	40	0.8	<0.4	NF	NF	NF	2.8
78. Idaho Falls, Idaho	2	3	3	NF	NF	NF	0.3
79. Corvallis, Oregon (Taylor Plant)	26	3	NF	NF	NF	NF	0.4
80. Ilwaco, Washington	167	35	5	NF	NF	NF	3.1
Range	<0.1-311	NF-116	NF-100	NF-92	NF-6	NF-3	<0.05-12.2

NF - None Found

TABLE 13

FREQUENCY DISTRIBUTION OF TRIHALOMETHANES

FINISHED WATER

	Chloroform		Bromodichloromethane		Dibromochloromethane		Bromoform	
Concentration Range, μg/l	% in Range	% ≤ Upper Conc.	% in Range	% ≤ Upper Conc.	% in Range	% ≤ Upper Conc.	% in Range	% ≤ Upper Conc.
NF	0	0	2.5	2.5	11.3	11.3	68.8	68.8
0-1	11.3	11.3	13.8	16.3	20.0	31.3	20.0	88.8
1.1-5	8.8	20.1	13.8	30.1	43.7	75.0	6.3	95.1
6-10	8.8	28.9	32.5	62.6	5.0	80.0	2.5	97.6
11-15	8.8	37.7	11.3	73.9	7.5	87.5	1.2	98.8
16-20	7.5	45.2	8.8	82.7	6.4	93.9	0	98.8
21-25	5.0	50.2	1.2	83.9	1.2	95.1	0	98.8
26-30	5.0	55.2	5.0	88.9	0	95.1	0	98.8
31-40	8.8	64.0	6.3	95.2	2.5	97.6	0	98.8
41-50	10.0	74.0	1.2	96.4	1.2	98.8	0	98.8
51-75	7.5	81.5	1.2	97.6	0	98.8	0	98.8
76-100	7.5	89.0	1.2	98.8	1.2	100.0	1.2	100.0
101-150								
151-200	2.5	97.5						
201-250	0	97.5						
251-300	0	97.5						
301-350	2.5	100.0						

NF = None found.

TABLE 13 (Cont'd.)

FREQUENCY DISTRIBUTION OF 1,2-DICHLOROETHANE AND CARBON TETRACHLORIDE

FINISHED WATER

1,2-Dichloroethane			Carbon Tetrachloride		
Concentration μg/l	% of Total	% ≤ Concentration	Concentration μg/l	% of Total	% ≤ Concentration
NF	67.5	67.5	NF	87.5	87.5
<0.2	12.4	79.9	<2	7.5	95.0
0.2	1.3	81.2	2	2.5	97.5
<0.3	1.3	82.5	3	2.5	100.0
0.3	1.3	83.8			
<0.4	11.2	95.0			
0.4	2.4	97.4			
2	1.3	98.7			
6	1.3	100.0			

NF = None found.

TABLE 13 (Cont'd.)

FREQUENCY DISTRIBUTION OF NON-VOLATILE TOTAL ORGANIC CARBON

FINISHED WATER

Concentration Range mg/l	% in Range	% ≤ Upper Concentration
<0.05	4.9	4.9
0.05-0.5	6.2	11.1
0.6-1.0	12.3	23.4
1.1-1.5	13.6	37.0
1.6-2.0	21.0	58.0
2.1-2.5	8.6	66.6
2.6-3.0	12.3	78.9
3.1-3.5	7.4	86.3
3.6-4.0	2.5	88.8
4.1-4.5	6.2	95.0
4.6-5.0	0	95.0
5.1-5.5	2.5	97.5
5.6-6.0	0	97.5
6.1-6.5	0	97.5
6.6-7.0	1.3	98.3
7.1-9.0	0	93.8
9.1-11.0	0	98.8
11.1-13.0	1.2	100.0

TABLE 14

Summary of Inorganic Analysis
All data in mg/l

	Nitrate AsNO$_3$	Barium	Arsenic	Selenium	Fluoride	Cyanide	Chromium	Silver	Lead	Cadmium	Mercur
1. Lawrence, Massachusetts	1.	<.2	<.005	<.005	.1	<.02	<.005	<.01	<.005	<.002	<.0005
2. Waterbury, Connecticut	2.	.02	<.005	<.005	.9	<.02	<.005	<.01	<.005	<.002	<.0005
3. Boston, Mass. (Metropolitan Dist. Comn.)	<1.	<.2	<.005	<.005	.1	<.02	<.005	<.01	<.005	<.002	<.0005
4. Newport, Rhode Island (Plant #1)	5.	.03	<.005	<.005	1.3	<.02	<.005	<.01	<.005	<.002	<.0005
5. New York, New York	1.	<.2	<.005	<.005	<.1	<.02	<.005	<.01	<.005	<.002	.0006
6. San Juan, P.R. (Sergio Cuevas Plant)	<1.	<.05	<.005	<.005	.5	<.02	<.005	<.01	<.005	<.002	.0015
7. Little Falls, N.J., Passaic Valley Water Comn.	2.	<.2	<.005	<.005	.1	<.02	<.005	<.01	.020	<.002	<.0005
8. Toms River, New Jersey	12.	<.05	<.005	<.005	<.1	<.02	<.005	<.01	.020	<.002	<.0005
9. Buffalo, New York	1.	.06	<.005	<.005	1.5*	<.02	<.005	<.01	<.005	<.002	<.0005
10. Rhinebeck, New York	2.	<.2	<.005	<.005	<.1	<.02	<.005	<.01	<.005	<.002	<.0005
11. Philadelphia, Pa. (Torresdale Plant)	4.	<.05	<.005	<.005	.9	<.02	<.005	<.01	.025	<.002	<.0005
12. Stanton, Delaware, Wilmington Suburban	7.	<.05	<.005	<.005	1.1	<.02	<.005	<.01	.014	<.002	.0022
13. Newark, Delaware, Artesian Water Company	NES	<.05	<.005	<.005	1.3	<.02	<.005	<.01	.040	.003	.0026
14. Washington, D.C., Wash. Aqueduct (Dalecarlia Plant)	4.	<.05	<.005	<.005	1.0	<.02	<.005	<.01	.005	<.002	<.0005
15. Baltimore, Maryland	3.	<.05	<.005	<.005	1.1	<.02	<.005	<.01	.008	<.002	<.0005
16. South Pittsburgh, Pa., West. Penn. Water Co., (Hays Mine Plant)	3.	<.2	<.005	<.005	1.4	<.02	<.005	<.01	.018	<.002	<.0005
17. Strasburg, Pennsylvania	12.	.08	<.005	<.005	.1	<.02	<.005	<.01	<.005	<.002	<.0005
18. Annandale, Va., Fairfax County Water Authority (New Lorton Plant)	2.	<.05	<.005	<.005	.8	<.02	<.005	<.01	.010	<.002	<.0005

Table 14 (Continued)

		Nitrate AsNO$_3$	Barium	Arsenic	Selenium	Fluoride	Cyanide	Chromium	Silver	Lead	Cadmium	Mercury
19.	Hopewell, Virginia ----------											
20.	Huntington, West Virginia ---	2.	<.2	<.005	<.005	.1	<.02	<.005	<.01	.070*	<.002	<.0005
21.	Wheeling, West Virginia -----	3.	<.2	<.005	<.005	1.4	<.02	<.005	<.01	<.005	<.002	<.0005
22.	Miami, Florida (Preston Plant) --------------------	<1.	.04	<.005	<.005	1.1	<.02	<.005	<.01	<.005	<.002	.0009
23.	Jacksonville, Florida -------	<1.	<.05	<.005	<.005	.7	<.02	<.005	<.01	.016	<.002	.0018
24.	Atlanta, Georgia (Chattahoochee Plant) ------------	1.	<.05	<.005	<.005	.7	<.02	<.005	<.01	.025	<.002	<.0005
25.	Owensboro, Kentucky ---------	<1.	.04	<.005	<.005	1.3	<.02	<.005	<.01	<.005	<.002	<.0005
26.	Greenville, Mississippi -----	<1.	.04	<.005	<.005	.5	<.02	<.005	<.01	<.005	<.002	<.0005
27.	Chattanooga, Tenn., Tenn. American Water Co. --------	1.	<.05	<.005	<.005	1.0	<.02	<.005	<.01	.010	<.002	.0028*
28.	Memphis, Tennessee ----------	<1.	<.05	<.005	<.005	<.1	<.02	<.005	<.01	.020	<.002	<.0005
29.	Nashville, Tennessee --------	2.	<.2	<.005	<.005	1.3	<.02	<.005	<.01	.010	<.002	<.0005
30.	Charleston, S.C. (Stoney Plant) -------------------											
31.	Cincinnati, Ohio ------------	2.	<.05	<.005	<.005	<.1	<.02	<.005	<.01	<.013	<.002	<.0005
32.	Chicago, Illinois (South Plant) -------------------	<1.	<.05	<.005	<.005	1.0	<.02	<.005	<.01	<.005	<.002	<.0005
33.	Clinton, Illinois -----------	<1.	.15	.013	<.005	1.0	<.02	<.005	<.01	.012	<.002	<.0005
34.	Indianapolis, Indiana (White River Plant) --------------	5.	.03	<.005	<.005	1.9*	<.02	<.005	<.01	.029	<.002	<.0005
35.	Whiting, Indiana ------------	2.	<.2	<.005	<.005	.1	<.02	<.005	<.01	<.005	<.002	<.0005
36.	Detroit, Michigan (Park Plant) -------------------	1.	<.2	<.005	<.005	1.1	<.02	<.005	<.01	<.005	<.002	<.0005
37.	Mt. Clemens, Michigan -------	<1.	.06	<.005	<.005	1.3	<.02	<.005	<.01	<.005	<.002	<.0005
38.	St. Paul, Minnesota	2.	<.2	<.005	<.005	1.3	<.02	<.005	<.01	.010	<.002	<.0005
39.	Cleveland, Ohio (Division Plant) -------------------	<1.	<.2	<.005	<.005	.1	<.02	<.005	<.01	.018	<.002	<.0005
40.	Columbus, Ohio (Dublin plant) -------------------	15.	<.2	<.005	<.005	1.4	<.02	<.005	<.01	.020	<.002	<.0005
41.	Dayton, Ohio (Ottawa Plant)--	5.	.04	<.005	<.005	.2	<.02	<.005	<.01	<.005	<.002	<.0005

Table 14 (Continued)

		Nitrate AsNO$_3$	Barium	Arsenic	Selenium	Fluoride	Cyanide	Chromium	Silver	Lead	Cadmium	Mercur.
42.	Indian Hill, Ohio ----------	5.	<.05	<.005	<.005	1.4	<.02	<.005	<.01	.016	<.002	<.0005
43.	Piqua, Ohio ----------------	8.	.03	<.005	<.005	.2	<.02	<.005	<.01	<.005	<.002	<.0005
44.	Youngstown, Ohio (Mahoning Valley San. Dist) --------	1.	<.05	<.005	<.005	1.0	<.02	<.005	<.01	.008	<.002	<.0005
45.	Milwaukee, Wisconsin (Howard Ave. Plant) -------------	1.	.04	<.005	<.005	.8	<.02	<.005	<.01	.024	<.002	<.0005
46.	Oshkosh, Wisconsin----------	2.	.02	<.005	<.005	1.0	<.02	<.005	<.01	<.005	<.002	<.0005
47.	Houma, La., Terrebonne Parrish Water Works #1 ---	<1.	.1	<.005	<.005	.1	<.02	<.005	<.01	.026	<.002	<.0005
48.	Camden, Arkansas -----------	1.	<.05	<.005	<.005	1.1	<.02	<.005	<.01	.013	<.002	<.0005
49.	Logansport, Louisiana ------	<1.	<.2	<.005	<.005	.1	<.02	<.005	<.01	.026	<.002	<.0005
50.	Albuquerque, New Mexico ----	<1.	.04	.01	<.005	1.3	<.02	<.005	<.01	<.005	<.002	<.0005
51.	Oklahoma City, Okla. (Hefner Plant) ------------------	<1.	<.05	<.005	<.005	.5	<.02	<.005	<.01	.017	<.002	<.0005
52.	Brownsville, Texas (Plant #2) ----------------------											
53.	Dallas, Texas (Bachman Plant) -------------------	2.	<.2	<.005	<.005	1.0	<.02	<.005	<.01	.014	<.002	<.0005
54.	San Antonio, Texas ---------	4.	<.2	<.005	<.005	0.1	<.02	<.005	<.01	<.005	<.002	NES
55a.	Ottumwa, Iowa --------------	8.	.07	<.005	<.005	1.3	<.02	<.005	<.01	.023	<.002	<.0005
56.	Clarinda, Iowa -------------	1.	<.05	<.005	<.005	.3	<.02	<.005	<.01	.025	<.005	<.0005
57.	Davenport, Iowa ------------	<1.	<.05	<.005	<.005	1.1	<.02	<.005	<.01	.012	<.002	<.0005
58.	Topeka, Kansas -------------	1.	<.2	<.005	<.005	1.2	<.02	<.005	<.01	<.005	<.002	<.0005
59.	Cape Girardeau, Mo., Mo. Utilities Co. ------------	5.	.08	<.005	<.005	1.1	<.02	<.005	<.01	<.005	<.002	<.0005
60.	Kansas City, Missouri ------	3.	.03	<.005	<.005	.1	<.02	<.005	<.01	<.005	<.002	<.0005
61.	St. Louis, Missouri, St. Louis County Wat. Co. (Central Plant) ----------	3.	.01	<.005	<.005	1.0	<.02	<.005	<.01	<.005	<.002	<.0005
62.	Lincoln, Nebraska ----------	<1.	<.2	<.005	<.005	1.1	<.02	<.005	<.01	<.005	<.002	<.0005
63.	Grand Forks, North Dakota --	2.	<.2	<.005	<.005	1.3	<.02	<.005	<.01	<.005	<.002	<.0005
64.	Denver, Colorado (North Side Marston Plant) -----------	<1.	<.2	<.005	<.005	1.3	<.02	<.005	<.01	<.005	<.002	<.0005

Table 14 (Continued)

	Nitrate AsNO3	Barium	Arsenic	Selenium	Fluoride	Cyanide	Chromium	Silver	Lead	Cadmium	Mercury
65. Pueblo, Colorado (Gardner Plant)	<1.	<.2	<.005	<.005	.6	<.02	<.005	<.01	<.005	.004	<.0005
66. Huron, South Dakota	<1.	<.2	<.005	<.005	1.6*	<.02	<.005	<.01	<.005	.003	<.0005
67. Salt Lake City, Utah (Parleys Plant)	<1.	<.05	<.005	<.005	.1	<.02	<.005	<.01	<.005	<.002	<.0005
68. Tuscon, Arizona (Plant #1)	3.	<.2	<.005	<.005	.8	<.02	<.005	<.01	.020	<.002	<.0005
69. Phoenix, Arizona (Verde Plant)	<1.	<.05	.005	<.005	.4	<.02	<.005	<.01	.017	<.002	<.0005
70. Coalinga, Calif. (Coalinga Mun. Water Plant)	2.	<.05	<.005	<.005	<.1	<.02	<.005	<.01	.018	<.002	<.0005
71. Concord, Cal., Contra Costa Cnty. Wat. Dist., (Bollman Plant)	2.	.08	<.005	<.005	1.2	<.02	<.005	<.01	<.005	<.002	<.0005
72. Dos Palos, California	3.	.08	<.005	<.005	<.1	<.02	<.005	<.01	.013	<.002	<.0005
73. Los Angeles, California (Owen's Aqueduct)	<1.	<.2	<.005	<.005	.7	<.02	<.005	<.01	<.005	<.002	<.0005
74. San Diego, California (Miramar Plant)	<1.	.04	<.005	<.005	.4	<.02	<.005	<.01	<.005	<.002	<.0005
75. San Francisco, Calif. (San Andreas Plant)	<1.	<.2	<.005	<.005	1.0	<.02	<.005	<.01	<.005	<.002	<.0005
76. Seattle, Washington (Cedar River)	<1.	.03	<.005	<.005	1.1	<.02	<.005	<.01	<.005	<.002	<.0005
77. Douglas, Alaska	<1.	<.2	<.005	<.005	<.1	<.02	<.005	<.01	<.005	<.002	<.0005
78. Idaho Falls, Idaho	<1.	.085	<.005	<.005	.2	<.02	<.005	<.01	.011	<.002	<.0005
79. Corvallis, Oregon (Taylor Plant)	<1.	<.2	<.005	<.005	1.2	<.02	<.005	<.01	.024	<.002	<.0005
80. Ilwaco, Washington	<1.	<.2	<.005	<.005	<.1	<.02	<.005	<.01	.018	<.002	<.0005

TABLE 15a

CONFIRMATION ANALYSIS DATA OF RAW WATER

(All data in μg/l)

Location	Chloroform	Bromodichloro-methane	Dibromochloro-methane	Bromoform	Carbon Tetrachloride	1,2 Dichloroethane
1. Waterbury, Connecticut	NF**	NF	NF	NF	NF	NF
	(0.2)	(NF)	(NF)	(NF)	(NF)	(0.31)
	(0.1)	(NF)	(NF)	(NF)	(NF)	(∼0.03)
2. Passaic Valley, New Jersey	0.3	NF	NF	NF	<2	<0.2
	(0.9)	(0.2)	(NF)	(NF)	(0.5)	(0.7)
	(0.4)	(NF)	(NF)	(NF)	(0.2)	(0.3)
16. South Pittsburgh, Pennsylvania	0.3	NF	NF	NF	NF	NF
	(1.2)	(NF)	(NF)	(NF)	(0.1)	(0.1)
	(0.4)	(NF)	(NF)	(NF)	(NF)	(NF)
30. Charleston, South Carolina	<0.2	NF	NF	NF	NF	NF
51. Oklahoma City, Oklahoma	NF	NF	NF	NF	NF	NF
	(0.5)	(NF)	(NF)	(NF)	(1.5)	(NF)
	(NF)	(NF)	(NF)	(NF)	(NF)	(NF)
60. Kansas City, Missouri	NF	NF	NF	NF	NF	NF
	(NF)	(NF)	(NF)	(NF)	(NF)	(NF)
	(NF)	(NF)	(NF)	(NF)	(NF)	(NF)

TABLE 15a (Cont'd.)

Location	Chloroform	Bromodichloro-methane	Dibromochloro-methane	Bromoform	Carbon Tetrachloride	1,2-Dichloroethane
65. Pueblo, Colorado	<0.2	NF	NF	NF	NF	NF
	(NF)	(NF)	(NF)	(NF)	(NF)	(NF)
	(NF)	(NF)	(NF)	(NF)	(NF)	(NF)
71. Contra Costa, California	0.3	<0.3	NF	NF	NF	NF
	(NF)	(NF)	(NF)	(NF)	(NF)	(NF)
	(NF)	(NF)	(NF)	(NF)	(NF)	(NF)
79. Corvallis, Oregon	NF	NF	NF	NF	NF	NF
	(0.5)	(NF)	(NF)	(NF)	(0.1)	(NF)
	(0.2)	(NF)	(NF)	(NF)	(0.1)	(NF)

NF = None found.

**The first listing of data is from the primary analysis performed by the method in section C(3)(a)(1), Part I. The data in parentheses () are from the quantitative confirmation analysis performed by the method in section C(3)(a)(1), Part II.

TABLE 15b

CONFIRMATION ANALYSIS DATA OF FINISHED WATER

(All Data in μg/l)

Location	Chloroform	Bromodichloro-methane	Dibromochloro-methane	Bromoform	Carbon Tetrachloride	1,2-Dichloroethane
1. Waterbury, Connecticut	93**	10	0.6	<1	<2	<0.2
	(61.6)	(5.5)	(NF)	(NF)	(0.5)	(NF)
	(61.2)	(5.6)	(NF)	(NF)	(0.5)	(NF)
2. Passaic Valley, New Jersey	59	16	2	NF	<2	<0.2
	(51.1)	(9.6)	(0.3)	(NF)	(0.4)	(NF)
	(35.9)	(7.4)	(NF)	(NF)	(0.3)	(NF)
11. Philadelphia, Pennsylvania***	86*	9*	5*	NF*	NF*	6*
16. South Pittsburgh, Pennsylvania	8	2	0.4	NF	NF	NF
	(10.7)	(1.5)	(0.2)	(NF)	(0.3)	(0.3)
	(9.2)	(1.5)	(NF)	(NF)	(0.1)	(0.2)
21. Wheeling, West Virginia	72	28	17	NF	NF	<0.4
22. Miami*** Florida	311*	78*	35*	3*	NF*	<0.2*
30. Charleston, South Carolina	195	9	0.8	0.8	NF	NF
31. Cincinnati, Ohio***	45*	13*	4*	NF*	<2*	<0.4*

TABLE 15b (Cont'd.)

Location	Chloroform	Bromodichloro-methane	Dibromochloro-methane	Bromoform	Carbon Tetrachloride	1,2-Dichloroethane
41. Dayton, Ohio	8	8	11	4	<2	<0.2
51. Oklahoma City, Oklahoma	44	28	20	6	<2	<0.4
	(40.1)	(23.8)	(13.5)	(NF)	(0.6)	(NF)
	(45.5)	(28.5)	(10.9)	( )	(0.8)	(NF)
55. Ottumwa, Iowa***	0.8*	NF*	NF*	NF	NF*	NF
58. Topeka, Kansas	88	38	19	5	3	NF
60. Kansas City, Missouri	24	8	2	NF	NF	NF
	(23.1)	(5.6)	(0.52)	(NF)	(0.3)	(NF)
Sample Lost	( )	( )	( )	( )	( )	( )
65. Pueblo, Colorado	2	2	<2	NF	NF	NF
	(1.9)	(0.8)	(NF)	(NF)	(0.3)	(NF)
	(1.8)	(0.8)	(NF)	(NF)	(0.3)	(NF)
66. Huron, South Dakota	309	116	49	8	NF	NF
71. Contra Costa, California	31	18	6	<1	NF	NF
	(25.1)	(11.9)	(2.3)	(NF)	(NF)	(NF)
	(26.7)	(12.4)	(2.1)	(NF)	(NF)	(NF)
72. Dos Palos, California	61	53	34	7	NF	NF

TABLE 15b (Cont'd.)

Location	Chloroform	Bromodichloro-methane	Dibromochloro-methane	Bromoform	Carbon Tetrachloride	1,2-Dichloroethane
76. Seattle, Washington***	15*	0.9*	NF*	NF	NF	NF
79. Corvallis, Oregon	26	3	NF	NF	NF	NF
	(23.0)	(1.6)	(NF)	(NF)	(0.2)	(NF)
	(18.6)	(1.2)	(NF)	(NF)	(0.1)	(NF)

NF = None found.

*Indicates a positive qualitative gas chromatography-mass spectrometry determination performed either by the method in section C(3)(a)(1), Part II or C(3)(c)(1).

**The first listing of data is from the primary analysis performed by the method in section C(3)(a)(1), Part I. The data in parentheses () are from the quantitative confirmation analysis performed by the method in section C(3)(a)(1), Part II.

***GC/MS data available for these supplies only at this time.

raw and finished waters in the 80 locations. Because of the increased sensitivity of the method described in Section C(3)(a)(1), Part II, analysis by that technique often produced a low measurable concentration where the routine method did not find the compound. This is not an inconsistency. The differences between the concentrations of the routine and confirmation analyses in a few cases is not considered to be significant.

b. Qualitative

The data in Table 15 shows that the compounds quantified by the routine analysis were the correct compounds. In no case did the routine analysis ever quantify a given compound and have a negative confirmation by gas chromatography-mass spectrometry (GC/MS). In few cases, because one of the GC/MS methods used a larger sample for purging, this technique would detect the presence of a compound when none was found by the routine procedure. This is not an inconsistency, and as noted above, the reverse did not occur.

4. Comprehensive 5-Location Organic Study

Three types of samples were collected from each of the First Series (Table 2) of locations for a comprehensive organic analysis. Work is still continuing on all of these 15 samples, therefore the results presented in the following tables must be considered preliminary. The complete analysis of these samples will be presented in the December report.

a. Groundwater, Miami, Florida

The Carbon-Chloroform Extract (CCE-m) concentration was 0.9 mg/l.

1) Selected Compound Analysis

TABLE 16

Organochlorine Pesticides	2 ng/l Dieldrin
Organophosphate Pesticides	None Found
Polychlorinated Biphenyls	None Found
Herbicides	None Found
Haloethers	None Found
Vinyl chloride - Raw	1.2 μg/l
- Finished	5.6 μg/l*

Sample collected 1/20/75.

*This value includes a trace amount of cyanogen chloride. The reason it is higher than the raw value is not known at this time.

2) Organics Purged from Grab Sample

See Table 17, next page.

3) Organics Extracted from Sample with Solvent

TABLE 18

Compounds Detected*	Approximate Concentration,** μg/l
Bromoform	0.2
Hexachloroethane	0.07
Di-n - octyl adipate	20.0
Nicotine	3.3

Sample collected 1/20/75

*List incomplete as samples are still being analyzed.

**Concentrations are probably accurate to within a factor of ten; with di-n-octyl adipate and nicotine, authentic samples were available and the concentrations of these are probably accurate to within ±50%.

4) Organics Adsorbed from Sample on Activated Carbon

See Table 19. All of these data were somewhat surprising initially, as ground water has traditionally been thought of as low in contaminants. These results may not apply to all ground waters, however, but may only be representative of areas with relatively high ground water tables and relatively shallow wells.

TABLE 17

Results reflect a single grab sample taken on January 20, 1975
in Miami, Florida

Compounds Found**

1. acetaldehyde
2. acetone
3. acetylenebromide
4. acetylenechloride
5. acetylenedichloride
*6. benzene
7. bromoform
8. bromomethane
9. carbon disulfide
10. carbon tetrachloride
*11. chlorobenzene
12. chloroethane
13. chloroform
14. chloromethane
15. cyanogen chloride
16. dibromochloromethane
17. m-dichlorobenzene
18. o-dichlorobenzene
*19. p-dichlorobenzene
20. dichlorobromomethane
21. 1,1 dichloroethane
22. 1,2 dichloroethane
*23. 1,1 dichloroethylene
(vinylidene chloride)
*24. cis-1,2 dichloroethylene
*25. trans 1,2 dichloroethylene
26. dichloromethane
27. methanol
28. 3-methyl butanal
29. 2-methyl butyl nitrile
30. 2-methyl propanal
31. 2-methyl propyl nitrile
*32. toluene
33. 1,1,2 trichloroethane
*34. trichloroethylene
*35. vinyl chloride

*Selected for future quantification.

**List incomplete as analysis is continuing. Any ambiguities in nomenclature will be corrected in the December 1975 report by using the systematic name as well as the common name.

TABLE 19

ORGANICS ADSORBED ON ACTIVATED CARBON FROM MIAMI, FLORIDA SAMPLE

	Compounds Found	Approximate Concentration in μg/liter
*1.	bromodichloromethane	4.5
*2.	bromoform	1.5
*3.	camphor	0.5
*4.	chlorobenzene	1
*5.	chlorodibromomethane	15
*6.	p-chlorotoluene	1.5
7.	cymeme isomer	0.1
*8.	2,6-di-t-butyl-p-benzoquinone	0.1
*9.	di-n-butyl phthalate	5
*10.	m-dichlorobenzene	0.5
*11.	p-dichlorobenzene	0.5
*12.	o-dichlorobenzene	1
*13.	diethyl phthalate	1
*14.	di-(2-ethylhexyl) phthalate	30
15.	di-n-propyl phthalate	0.5
*16.	hexachloroethane	0.5
*17.	n-propylbenzene	0.05
18.	n-propylcyclohexanone	0.2
*19.	tetrachloroethylene	0.1
20.	1,1,3,3-tetrachloro-2-propanone	0.2
21.	tetramethylbenzene isomer	0.2
*22.	tri-n-butyl phosphate	0.5

*Confirmed by comparison of MS and RRT with standard.

b. Uncontaminated Upland Water, Seattle, Washington

The carbon chloroform extract (CCE-m) of this water was 0.1 mg/l.

1) Selected Compound Analysis

TABLE 20

Organochlorine Pesticides	1 ng/l Dieldrin
Organophosphate Pesticides	None Found
Polychlorinated Biphenyls	None Found
Herbicides	None Found
Haloethers	None Found
Vinyl Chloride - Raw	None Found
- Finished	None Found

Sample collected 1/27/75

2) Organics Purged from Grab Sample

TABLE 21

RESULTS REFLECT A SINGLE GRAB SAMPLE

TAKEN ON JANUARY 27, 1975, IN SEATTLE, WASHINGTON

Compounds Found*

1. acetaldehyde
2. acetone
3. 2-butanone
4. chloroform
5. dibromochloromethane
6. dichlorobromomethane
7. dichloromethane
8. ethanol
9. methanol
10. methyl acetate
11. methyl ether
12. methyl formate
13. 2-methyl propanal

---

*List incomplete as analysis is continuing. Any ambiguities in nomenclature will be corrected in the December 1975 report by using the systematic name as well as the common name.

3) Organics Extracted from Sample by Solvent

None found (sample collected 1/27/75).

4) Organics Adsorbed from Sample on Activated Carbon

TABLE 22

ORGANICS ABSORBED ON ACTIVATED CARBON

FROM SEATTLE, WASHINGTON SAMPLE

Compounds Found	Approximate Concentration in μg/l liter
*1. acetaldehyde	0.1
*2. acetone	1
*3. bromodichloromethane	0.1
*4. camphor	0.5
*5. chloral (trichloroacetaldehyde)	3.5
*6. di-n-butyl phthalate	0.01
*7. diethyl phthalate	0.01
8. p-ethyltoluene	0.05
9. β-santalene	0.01

---

*Confirmed by comparison of MS and RRT with standard.

c. Raw Water Contaminated by Agricultural Runoff, Ottumwa, Iowa

The carbon-chloroform extract (CCE-m) concentration of this water was 0.7 mg/l.

1) Selected Compound Analysis

TABLE 23

Organochlorine Pesticides	2ng/l Dieldrin
Organophosphate Pesticides	None Found
Polychlorinated Biphenyls	None Found
Herbicides	None Found
Haloethers	None Found
Vinyl Chloride - Raw	None Found
- Finished	None Found

Sample collected 2/25/75.

2) Organics Purged From Grab Sample

TABLE 24

Results reflect a single grab sample

taken on February 2, 1975 in Ottumwa, Iowa

Compounds Found**

1. acetaldehyde
2. acetone
*3. benzene
4. 2-butanone
5. carbon tetrachloride
6. chloroform
7. chloromethane
8. cyanogenchloride
9. dibromochloromethane
10. dichlorobromomethane
11. dichloromethane
12. dimethyl disulfide
13. ethanol
14. 3 methyl butanal
15. 3-methyl-2-butanone
16. 2-methyl propanal
*17. toluene
18. 1,1,1 trichloroethane
*19. trichloroethylene

---

*Selected for future quantification.

**List incomplete as analysis is continuing. Any ambiguities in nomenclature will be corrected in the December 1975 report by using the systematic name as well as the common name.

3) Organics Extracted from Sample with Solvent

TABLE 25

Compounds Found**	Approximate Concentration, µg/l*
Benzoic Acid	15
Phenylacetic Acid	4

Sample collected 2/17/75.

---

*List incomplete as analysis is continuing.

**Concentrations are probably accurate to within a factor of ten; with benzoic acid authentic samples were available and the concentrations of this are probably accurate to with ±50%.

4) Organics Adsorbed from Sample on Activated Carbon

TABLE 26

Compounds Found		Approximate Concentration in μg/liter
*1.	atrazine	0.1
*2.	camphor	0.1
*3.	chloropicrin (trichloronitromethane)	0.05
*4.	cyclohexanone	0.1
*5.	di-n-butyl phthalate	0.1
6.	3-methyl-3-pentanal	1
7.	n-pentanal	0.5
*8.	2-pentanone	0.1
*9.	α-terpeneol	0.5
10.	tetramethyltetrahydrofuran	0.5

*Confirmed by comparison of MS and RRT with standard.

d. Raw Water Contaminated by Municipal Dishcarges, Philadelphia, Pennsylvania

The carbon chloroform extract (CCE-m) concentration of this water was 0.4 mg/l.

1) Selected Compound Analysis

TABLE 27

Organochlorine Pesticides	None Found
Organophosphate Pesticides	None Found
Polychlorinated Biphenyls	None Found
Herbicides	None Found
Haloethers	0.4 μg/l Bis-2 (chloroethyl)ether*
Resample 3/31/75	0.5 μg/l Bis-2 (chloroethyl)ether
Vinyl Chloride - Raw	None Found
- Finished	0.27 μg/l**

Sample collected 2/3/75

*Confirmed qualitatively by mass spectrometer.

**This value represents a combination of vinyl chloride and cyanogen chloride. Mass spectrometer analysis indicates a greater amount of cyanogen chloride than vinyl chloride. The reason the finished water value is higher than the raw water value is not known at this time.

Table 28

Results reflect a single grab sample taken on February 3, 1975, in Philadelphia, Pennsylvania.

Compounds Found**

1. acetaldehyde
2. acetone
3. acetylenechloride
4. acetylene dichloride
*5. benzene
6. bromoform
7. 2-butanone
8. carbon tetrachloride
*9. chlorobenzene
10. chloroethane
11. chloroform
12. chloromethane
13. cyanogenchloride
14. dibromochloromethane
15. m-dichlorobenzene
16. o-dichlorobenzene
*17. p-dichlorobenzene
18. dichlorobromomethane
19. 1,2 dichloroethane
20. 1,1 dichloroethylene
*21. cis,1, 2 dichloroethylene
22. dichloromethane
23. dimethoxymethane
24. ethanol
25. ethyl ether
26. methanol
27. 3-methyl butanal
28. 2-methyl butyl nitrile
29. methyl ether
30. 2-methyl propanal
31. 2-methyl propyl nitrile
32. nitromethane
*33. tetrachloroethylene
*34. toluene
*35. trichloroethylene
*36. vinyl chloride

---

*Selected for future quantification

**List incomplete as analysis is continuing. Any ambiguities in nomenclature will be corrected in the December 1975 report by using the systematic name as well as the common name.

2) Organics Purged from Grab Sample

See Table 28 on next page.

3) Organics Extracted from Sample by Solvent

TABLE 29

Compound Found*	Approximate Concentration,** µg/l
1,2-Bis(2-chloroethoxy)ethane	0.03

Sample collected 2/3/75

*List incomplete as analysis is continuing.

**Concentration is probably accurate to within a factor of ten.

4) Organics Adsorbed from Sample on Activated Carbon

TABLE 30

	Compounds Found	Approximate Concentration in µg/l
*1.	acetaldehyde	0.1
*2.	acetophenone	1
*3.	bromodichloromethane	1
4.	t-butyltoluene	0.01
*5.	chloral (trichloroacetaldehyde)	5
*6.	chlorodibromomethane	0.5
*7.	di-n-butyl phthalate	0.05
*8.	diethyl phthalate	0.01
*9.	di-(2-ethylhexyl) phthalate	0.5
10.	1,1,3,3-tetrachloro-2-propanone	1

*Confirmed by comparison of MS and RRT with standard.

e. Raw Water Contaminated with Industrial Discharges, Cincinnati, Ohio

The carbon chloroform extract (CCE-m) concentration of this water was 0.7 mg/l.

1) Selected Compound Analysis

TABLE 31

Organochlorine Pesticides	1 ng/l Dieldrin
Organophosphate Pesticides	None Found
Polychlorinated Biphenyls	None Found
Herbicides	None Found
Haloethers	None Found
Vinyl Chloride - Raw	None Found
- Finished	None Found

Sample collected 2/11/75.

2) Organics Purged from Grab Sample

See Table 32 on next page.

3) Organics Extracted from Sample by Solvent

TABLE 33

Compounds Found**	Approximate Concentrations,* in μg/l
Dibromochloromethane	0.05
Isophorone	0.02
Trimethyl isocyanurate	0.02

Sample collected 2/11/75.

*Concentrations are probably accurate to within a factor of ten.

**List incomplete as analysis is continuing.

4) Organics Adsorbed from the Sample on Activated Carbon

See Table 34.

Table 32

Results reflect a single grab sample taken on February 11, 1975, in Cincinnati, Ohio.

Compounds Found**

1. acetaldehyde
2. acetone
3. acetylenechloride
4. acetylene dichloride
*5. benzene
6. bromoform
7. 2-butanone
8. carbon disulfide
9. carbon tetrachloride
*10. chlorobenzene
11. chloroethane
12. chloroform
13. chloromethane
14. cyanogenchloride
15. dibromochloromethane
16. m-dichlorobenzene
17. o-dichlorobenzene
*18. p-dichlorobenzene
19. dichlorobromomethane
20. 1,2 dichloroethane
21. 1,1 dichloroethylene
*22. cis, 1,2 dichloroethylene
23. dichloromethane
24. ethanol
25. ethyl ether
26. methanol
27. 3-methyl butanal
28. 2-methyl butyl nitrile
29. methyl ether
30. 2-methyl propanal
31. 2-methyl propyl nitrile
32. nitromethane
***33. nitrotrichloromethane (chloropicrin)
*34. tetrachloroethylene
*35. toluene
*36. trichloroethylene

---

*Selected for future quantification.

**List incomplete as analysis is continuing. Any ambiguities in nomenclature will be corrected in the December 1975 report by using the systematic name as well as the common name.

***Alternate for future quantification.

TABLE 34

ORGANICS ADSORBED ON ACTIVATED CARBON FROM CINCINNATI, OHIO SAMPLE

	Compounds Found	Approximate Concentration in μg/liter
*1.	bromodichloromethane	1
*2.	camphor	0.1
*3.	chloral (trichloroacetaldehyde)	2
*4.	chlorodibromomethane	0.5
*5.	diethyl malonate	0.01
*6.	diethyl phthalate	0.1
*7.	lindane (γ BHC)	0.01
*8.	n-propylbenzene	0.01
*9.	tetrachloroethylene	0.1
10.	1,1,3,3-tetrachloro-2-propanone	0.5
*11.	tri-n-butyl phosphate	0.05
*12.	1,3,5-trimethyl-2,4,6-trioxo-hexa-hydrotriazine	0.5

*Confirmed by comparison of MS and RRT with standard.

E. DISCUSSION

1. Are Trihalomethanes Formed by Chlorination and If So, How Widespread is Their Occurrence?

a. Trihalomethanes

The first objective of the national Organics Reconnaissance Survey was to determine the extent of chlorination by-products in finished drinking water as reported by Rook[17] and Bellar, Lichtenberg and Kroner.[18] To meet this objective, raw and finished water from 80 locations, representing a wide variety of raw water sources and water treatment practices, were sampled for the four trihalomethanes -- chloroform, bromodichloromethane, dibromochloromethane, and bromoform.

In general, these four compounds were absent from the raw waters tested or were present in concentrations of less than 1 μg/l. Therefore, the presence of any of these four compounds in the finished water was concluded to be caused by chlorination practices.

None of the systems investigated did not disinfect, but one system practiced ozonation as the only treatment the water received. All of the finished waters tested contained some chloroform although the system described above only contained 0.1 μg/l. Although a number of finished waters did not contain bromodichloromethane, dibromochloromethane and bromoform, the presence of these compounds were concluded to be widespread throughout the finished waters of the nation.

Although the range of concentrations found for each of the four trihalomethanes was wide for the type of systems surveyed, the concentrations of each of the compounds was not evenly distributed throughout the range but were grouped toward the lower end of the range. Note: Many ground water supplies in the United States do not chlorinate and therefore would not contain any trihalomethane, but none of these supplies were included in the Survey. Based on Figure 2, the theoretical finished water with the median concentration (one-half of the data above and below) of each compound, would contain about 21 μg/l of chlorofrom, 6 μg/l of bromodichloromethane, 1.2 μg/l of dibromochloromethane, and bromoform below the detection limit of the analytic method used. Therefore, although the presence of these compounds was widespread, in many of the finished waters tested in this survey their concentrations were fairly low.

Although most of the finished waters had concentrations of the four trihalomethanes declining in the same order as those in the theoretical "median" water described above, this was not true in all cases. The reasons for concentrations of the heavier compounds being greater than the lighter ones in some finished water are not known. Rook[17] has postulated that if bromide was present in a water, the chlorine will oxidize the bromide to bromine and the heavier bromo-compounds would be formed. Whether this phenomenon occurred in some of the finished waters surveyed is not known.

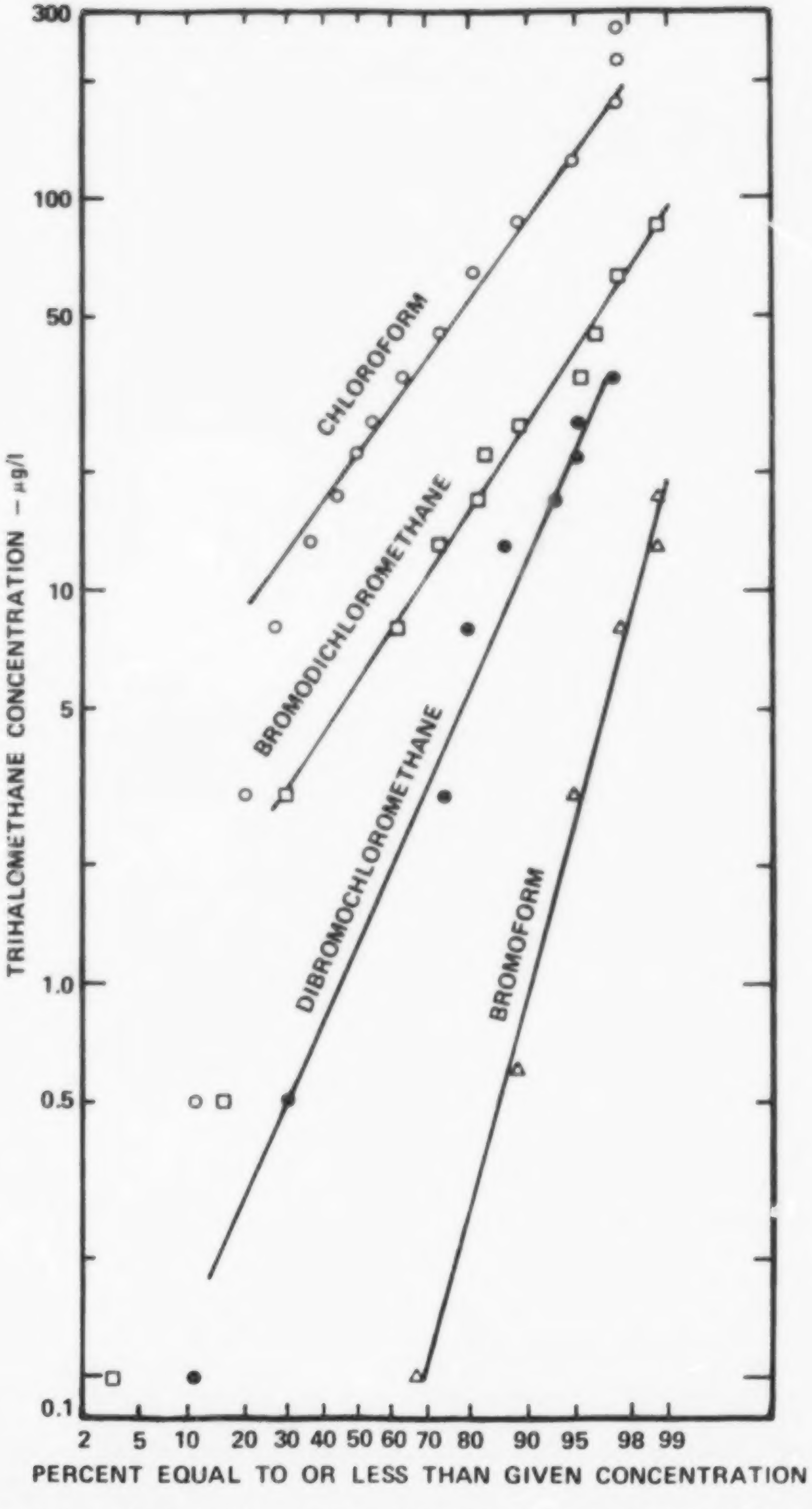

FIGURE 2. FREQUENCY DISTRIBUTION OF TRIHALOMETHANE DATA

b. 1,2-Dichloroethane and Carbon Tetrachloride

Analysis was also made of all samples for 1,2-Dichloroethane and carbon tetrachloride because they had been found in other drinking waters previously and had potential health significance. In this Survey, these two compounds were mostly absent from finished water. In about one-third of the cases where these compounds were present in the finished water, they were also present in the raw water, indicating they were environmental contaminants and were not created during water treatment. The cause for the appearance of these compounds in the finished water when they were absent from the raw water is not known at this time.

c. Non-Volatile Total Organic Carbon

In addition to studying the six specific compounds discussed above, an attempt was made to investigate the general organic level in finished drinking waters by measuring the non-volatile total organic carbon (NVTOC) concentration in all 80 locations. The range of these data was from less than 0.05 mg/l to 12.2 mg/l, but again, the data were grouped toward the lower end of the range, see Figure 3. The median NVTOC concentration (one-half of the data above and below) was 1.5 mg/l.

2. Influence of Source Type and Treatment Practice on Trihalomethane Formation

The second objective of the Survey was to determine, if possible, the influence of type of source and treatment practiced on the formation of chlorination by-products. An initial examination of the data indicated that the dominant factor influencing the creation of chlorination by-products was the general organic level of the water, provided sufficient chlorine was added to satisfy the chlorine demand.

To test this hypothesis, the total trihalomethane concentration was first calculated for each finished water. This was done by dividing each of the four concentrations by the appropriate molecular weight and adding the quotients together. This yielded a total trihalomethane (TTHM) concentration in μMoles/liter.* These data were then plotted against the NVTOC concentration of the finished water. The TTHM data was divided into NVTOC cells in ascending order, each cell having a range of 0.5 mg/l NVTOC. The average TTHM concentration was then calculated for each cell and plotted against the appropriate NVTOC concentration. This analysis is appropriate based on the assumption that each cell is sufficiently large and heterogeneous with respect to the other variables that their influence is damped out by the averaging process.

During this analysis, the raw water NVTOC concentration was considered to be a better measure of the level of precursor available to react

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*Note: 1 μM/l TTHM = 119 μg/l chloroform if only chloroform was present.

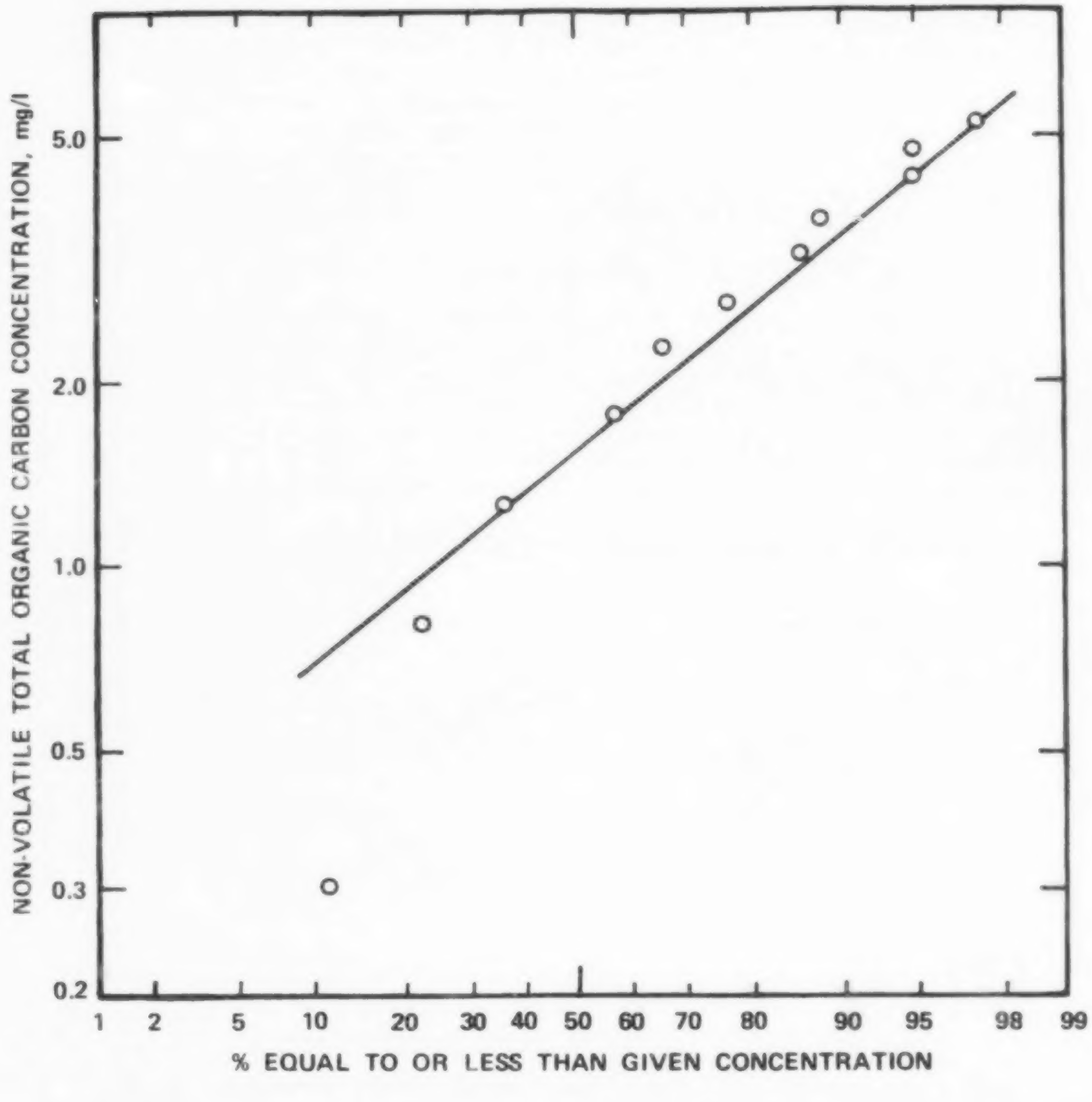

FIGURE 3. FREQUENCY DISTRIBUTION OF NON-VOLATILE TOTAL ORGANIC CARBON DATA

with the chlorine than the finished water NVTOC, particularly in situations where pre-chlorination is practiced, but the raw water NVTOC data contained a negative error because of the incomplete combustion of suspended material in the analytic procedure and could not be used. Analysis of the data showed, however, that finished water NVTOC could be used as an indicator of precursor level because raw- and finished-NVTOC concentrations are proportional to one another.*

The good correlation in Figure 4 shows that because most finished waters contain a residual, meaning an excess of one of the reactants is present, the concentration of the product (TTHM) is related to the concentration of the other reactants (unknown precursors) and further that the NVTOC concentration is a reasonable indication of their concentrations.

All of the data were then divided into four NVTOC concentration cells, 0-1 mg/l, 1-2 mg/l, 2-3 mg/l, and greater than 3 mg/l to eliminate the influence of that variable and then sorted so that like source types and treatment practices were in the same cells.

a. Source Influence

In the NVTOC 0-1 mg/l cell, ground water sources had lower average TTHM concentrations than surface waters. Considering all NVTOC cells not much difference existed between the various types of surface water.

TABLE 30

SOURCE INFLUENCE

NVTOC Range	n	0-1 mg/l Avg. TTHM Conc. μM/l	n	1-2 mg/l Avg. TTHM Conc. μM/l	n	2-3 mg/l Avg. TTHM Conc. μM/l	n	>3 mg/l Avg. TTHM Conc. μM/l
All Locations	18	0.15	20	0.35	10	0.56	10	1.07
Ground Water	9	0.07	1	0.32	1	0.11	2	1.65
River Water	7	0.25	10	0.47	5	0.60	2	0.98
Lake and Reservoir Water	2	0.21	9	0.21	4	0.61	6	0.90

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*Based on these data, coagulation and filtration removed about 30% of the raw NVTOC on the average, but this percentage is probably low.

b. Treatment Influence

1) Chlorination Practice

TABLE 31

CHLORINATION PRACTICE INFLUENCE

NVTOC Range	n	0-1 mg/l Avg. TTHM Conc. µM/l	n	1-2 mg/l Avg. TTHM Conc. µM/l	n	2-3 mg/l Avg. TTHM Conc. µM/l	n	>3 mg/l Avg. TTHM Conc. µM/l
All Locations	18	0.15	20	0.35	10	0.56	10	1.07
Prechlorination	10	0.23	17	0.36	8	0.58	7	1.33
No Prechlorination	8	0.05	3	0.28	2	0.48	3	0.45
Little or no Free Residual	8	0.10	5	0.15	5	0.40	5	0.71
Little or No Combined Residual >0.4 mg/l Free Residual	7	0.21	11	0.34	3	0.70	3	1.68

In all NVTOC cell locations where prechlorination was practiced higher average TTHM concentrations resulted than where no preclorination was practiced. An attempt was made to relate prechlorine dose to average TTHM production, but the number of locations in each cell was too small to produce meaningful data. The trend of average TTHM production was generally higher as prechlorine dose increased, but the data were quite variable. The data on chlorine residual indicated that finished waters that did not contain much free chlorine residual had lower TTHM concentrations than systems that had higher free chlorine residuals. The two locations using ozone had very low concentrations of TTHM. In Whiting, Indiana pre-ozonation is used following pre-chlorination. Whether or not the reduction in TTHM concentration following ozonation is caused by simple stripping or reaction of the ozone with the trihalomethanes is not known at this time. In the other installation, Strasburg, Pennsylvania, not only was ozonation the only treatment, but also the NVTOC concentration was only 0.05 mg/l. Both of these factors may have contributed to the low TTHM concentration.

2) Filtration Practice

All of the locations that practice filtration were sorted into NVTOC concentration cells and then re-sorted based on the use of polyelectrolyte either as a coagulant or filter-aid. Surface water was the raw water source for 90% of these plants, so that variable is essentially removed. This was to determine whether or not polyelectrolyte could aid as a precursor for TTHM formation. In the study group, the polyelectrolyte dose varied from 0.02 mg/l to 3.94 mg/l (1.27 mg/l in the raw water, plus 2.67 mg/l on the filters) on the days of sampling. At two locations the dose was unknown. Table 32 shows that the use of polyelectrolyte does not enhance TTHM formation.

TABLE 32

INFLUENCE OF FILTRATION PRACTICE

		0-1 mg/l		1-2 mg/l		2-3 mg/l		>3 mg/l
NVTOC Range	n	Avg. TTHM Conc. μM/l	n	Avg. TTHM Conc. μM/l	n	Avg. TTHM Conc. μM/l	n	Avg. TTHM Conc. μM/l
All	18	0.15	20	0.35	10	0.56	10	1.07
All Filter Plants	10	0.23	18	0.38	7	0.61	10	1.07
With Polyelectrolytes	4	0.26	4	0.42	2	0.81	2	1.28
Without Polyelectrolytes	6	0.21	14	0.37	5	0.53	8	1.01

3) Use of Activated Carbon

A. Powdered

Of the treatment plants using powdered activated carbon the dosage varied from 0.6 mg/l to 6.5 mg/l. All of these plants were surface water plants. Table 33 shows that, in NVTOC concentration cells where sufficient numbers exist for comparison purposes, locations where powdered activated carbon was used had average TTHM concentrations similar to those locations without powdered activated carbon. Either powdered activated carbon cannot remove trihalomethane precursors or the dosages used were insufficient to accomplish this.

TABLE 33

INFLUENCE OF POWDERED ACTIVATED CARBON

NVTOC Range	n	0-1 mg/l Avg. TTHM Conc. μM/l	n	1-2 mg/l Avg. TTHM Conc. μM/l	n	2-3 mg/l Avg. TTHM Conc. μM/l	n	>3mg/l Avg. TTHM Conc. μM/l
All	18	0.15	20	0.35	10	0.56	10	1.07
All Filter Plants	10	0.23	18	0.38	7	0.61	10	1.07
With Powdered Activated Carbon	2	0.31	5	0.42	5	0.58	3	0.45
Without Powdered Activated Carbon	7	0.20	11	0.35	5	0.58	5	1.35

B. Granular

Only six water treatment plants used granular activated carbon as a combination filtration/adsorption media, and this number is too small to make an analysis as above. All treat surface water, pre-chlorinate, and all but one had >0.4 mg/l free residual in the finished water, so some of the variables noted above were eliminated. Because all of the locations originally sampled were using granular activated carbon that had been in place for at least several months, the activated carbon was exhausted for NVTOC removal. This is shown in Table 34; the average NVTOC removal at these locations was not much higher than equal to or greater than 30 percent NVTOC removal previously reported for all coagulation-filtration plants. Therefore the TTHM concentration in these finished waters being higher than the TTHM concentration in the theoretical "median" finished water for the entire survey in 5 out of 6 locations is not surprising. This is also true when the data are examined on a "TTHM production per unit of NVTOC" basis.

Shortly after the Survey samples were taken at one of these locations, the granular activated carbon was removed and replaced with virgin lignite-base material. This location was resampled in an effort to evaluate the performance of fresh granular activated carbon. The data in Table 34 show a marked improvement in all three of the parameters listed indicating the effectiveness of fresh granular activated carbon for treatment.

Another attempt was made to evaluate the performance of granular activated carbon for treating a variety of waters by monitoring the activated carbon (CAM) units installed in the five locations where the samples of organics that could be adsorbed on activated carbon from

Table 34

SUMMARY OF GRANULAR ACTIVATED CARBON PLANTS

Location	Finished Water NVTOC Conc. mg/l	% Removal of NVTOC	TTHM Concentration µM/l	TTHM/ Fin. NVTOC µM/mg
20	1.0	≥55	0.31	0.31
37	1.4	≥30	0.41	0.10
1	1.6	≥56	0.82	0.51
47	3.2	≥41	1.36	0.43
43	4.2	≥30	1.19	0.28
57	4.4	≥32	0.79	0.18
Avg.		≥41		0.30
Theo. Median Water*	1.5	-	0.22	0.15
Fresh Gran. Act. Carbon	1.4	≥79	0.08	0.06

*See Figures 2 and 3 for median concentration.

finished waters were being collected. The samplers were 3-foot columns of coal-based granular activated carbon operated downflow at an approach velocity of 3.2 gallons per minute/square foot, and finished water was passed through them for seven days. The empty bed contact time was about 7 minutes. Table 35 shows that fresh granular activated carbon produced low NVTOC concentrations at first in all locations except Miami where the load was so heavy that a longer contact time would be needed to produce a lower NVTOC concentration.

c. Section Summary

To test the hypothesis that the use of surface water as a source, pre-chlorination, and the presence of greater than 0.4 mg/l free chlorine residual enhances the formation of trihalomethanes, the data were sorted on that basis. Out of the entire survey 28 locations met these three criteria.

TABLE 35

PERFORMANCE OF FRESH COAL-BASED GRANULAR ACTIVATED CARBON SAMPLERS

TREATING FINISHED WATER

Location	Day	NVTOC Concentration - mg/l Influent to Sampler	Effluent from Sampler	NVTOC Removed
Miami, Florida	0	8.1	1.3	84%
	7	7.1	3.5	51%
Seattle, Washington	0	1.9	1.9*	0%*
	7	0.8	0.05	94%
Ottumwa, Iowa	0	3.6	1.6*	56%*
	7	3.4	0.9	73%
Philadelphia, Pennsylvania	0	2.0	0.3	85%
	7	1.9	0.5	74%
Cincinnati, Ohio	0	1.2	0.1	92%
	7	1.6	0.1	94%

*Data Suspect.

Of these, 10 finished waters had an NVTOC concentration less than the Survey median concentration of 1.5 mg/l, the remainder being equal to or greater than the median. Of those with a finished water NVTOC concentration below the median concentration, 80% had a TTHM concentration above the median TTHM concentration. While of those with a finished water NVTOC concentration equal to or greater than the median concentration, only 11% had TTHM concentrations below the median TTHM concentration.

While this indicates the general validity of the proposed hypothesis, a rigorous multiple regression analysis of the data would be helpful. This analysis will be included in the December 1975 report.

3. Alternate Indicators of Organic Contaminant Levels

Because various organic contaminants vary in toxicity, specific organic compounds should be monitored in finished waters. This is the recommended procedure for monitoring organochlorine pesticides, for example. Except for a few specific examples, this approach is beyond the capabilities of most water utilities and to some degree even is beyond the capabilities of researchers, given the current state of organic analysis. All specific organic compounds present in water cannot now be identified and quantified.

In the absence of measuring for specific organic compounds, the next best alternative is to measure some organic parameter that includes a large number of organic compounds and assume that the level of this parameter is proportional to the level of toxicity of the water. On this basis carbon chloroform extract (CCE-m) was included in the Interim Primary Drinking Water Regulation.

In the National Organics Reconnaissance Survey non-volatile total organic carbon was the parameter chosen to represent the concentration of organics in the water. Figure 4 shows NVTOC to be generally proportional to trihalomethane formation, so a measure such as this is probably useful, but little else is known about NVTOC.

In an effort to find an easier analytic procedure for monitoring the organic level in water, three other measurements were made on each raw and finished water in addition to NVTOC concentration. These were ultraviolet absorption (UV), emission fluorescence scan (EmFC), and the Rapid Fluorometric Method (RFM). An attempt was made to correlate these parameters, even though different organics absorb ultraviolet to differing degrees and some different organics fluoresce to differing degrees. Therefore, although the *a priori* judgment was that those three parameters might not correlate with NVTOC concentrations because they would be heavily influenced by the types of organics present in the water, the hypothesis that different waters would be sufficiently similar to make these procedures useful was tested.

Just as particulates in some raw waters interfered with the NVTOC measurement, the resultant turbidity interfered with the UV, EmFS, and RFM measurements. Plots of NVTOC concentration versus each parameter

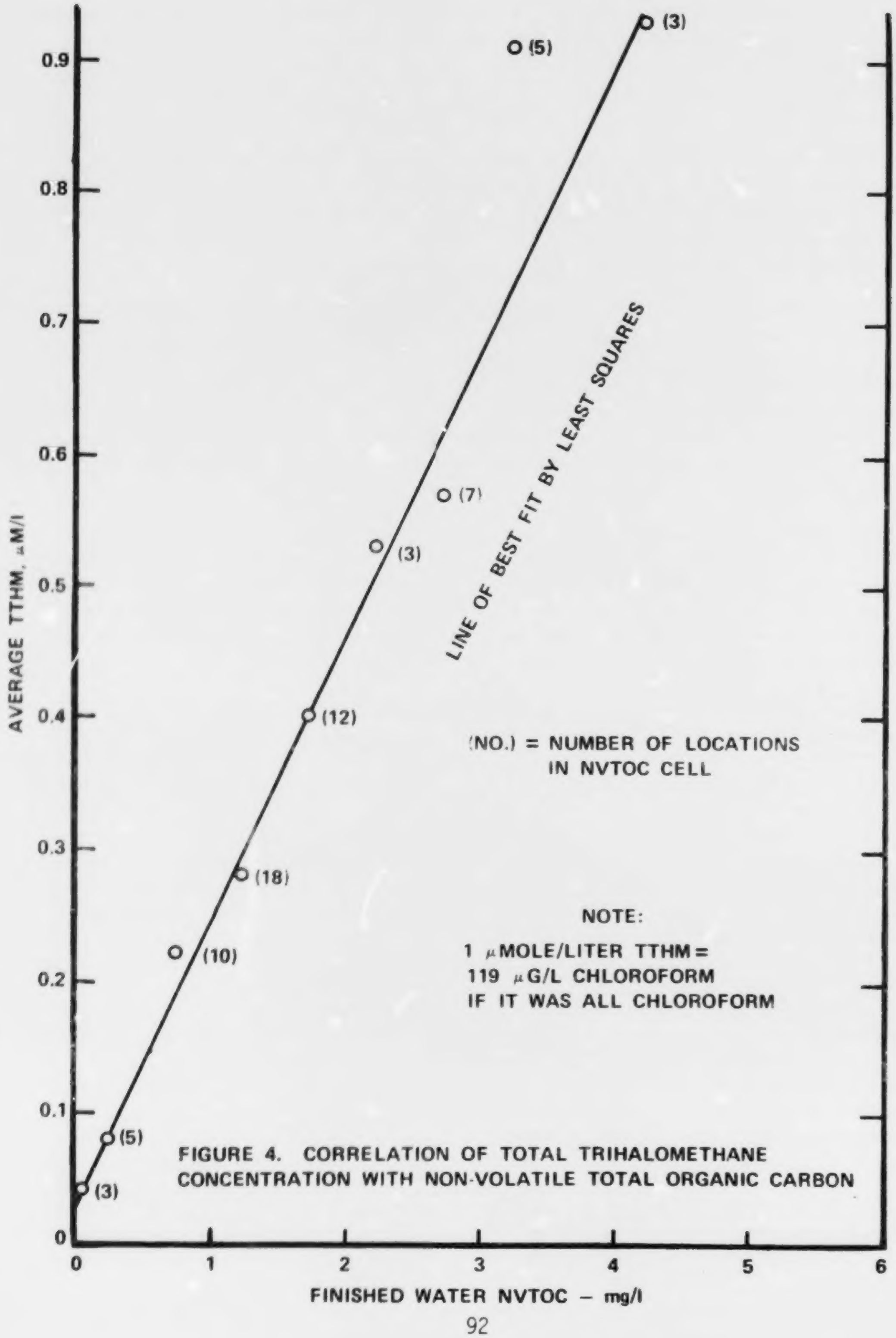

FIGURE 4. CORRELATION OF TOTAL TRIHALOMETHANE CONCENTRATION WITH NON-VOLATILE TOTAL ORGANIC CARBON

for finished water, Figures 5, 6, and 7 show a wide scatter of data. On Figure 5 a band 1 mg/l of NVTOC wide includes 39 data points, while only excluding 28 data points, up to an NVTOC concentration of 3.5 mg/l, but the overall correlation is not very good. The two fluorescence techniques correlated well with each other but not with NVTOC concentration.

4. Organics Found in the 5-Location Study

Because the qualitative results are incomplete and the quantitative results are absent, these data cannot be discussed, except to note that thus far the upland water and the water contaminated by agricultural runoff have had the fewest organics identified from them.

5. Significance of Findings

Most water treatment plants are not designed to remove soluble organic compounds from raw water, and disinfection creates some compounds that were not originally present in the raw water. Therefore, the finding that all finished waters in the Survey contained one type of organic compound or another should not be surprising. The presence of an organic compound in a finished water is not significant, however, unless its concentration is such that it poses a health hazard. The data contained in Appendix II, therefore, must be combined with that in Appendix VII, "Health Effects Caused by Exposure to Drinking Water Contaminants" before any significance can be attached to the data contained herein. If a health hazard is found to exist with any contaminant, then the treatment information contained in Appendix VI must be applied.

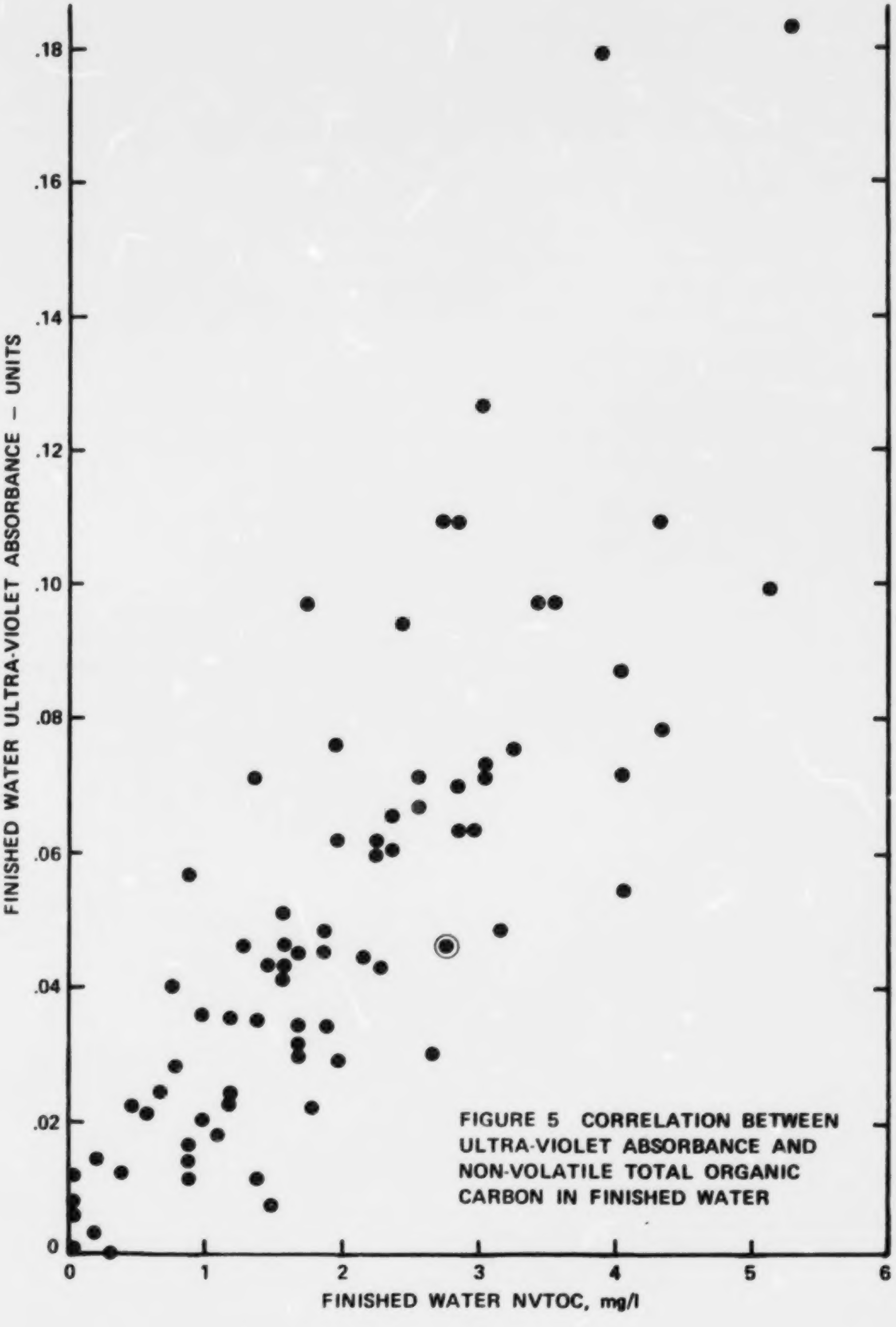

FIGURE 5 CORRELATION BETWEEN ULTRA-VIOLET ABSORBANCE AND NON-VOLATILE TOTAL ORGANIC CARBON IN FINISHED WATER

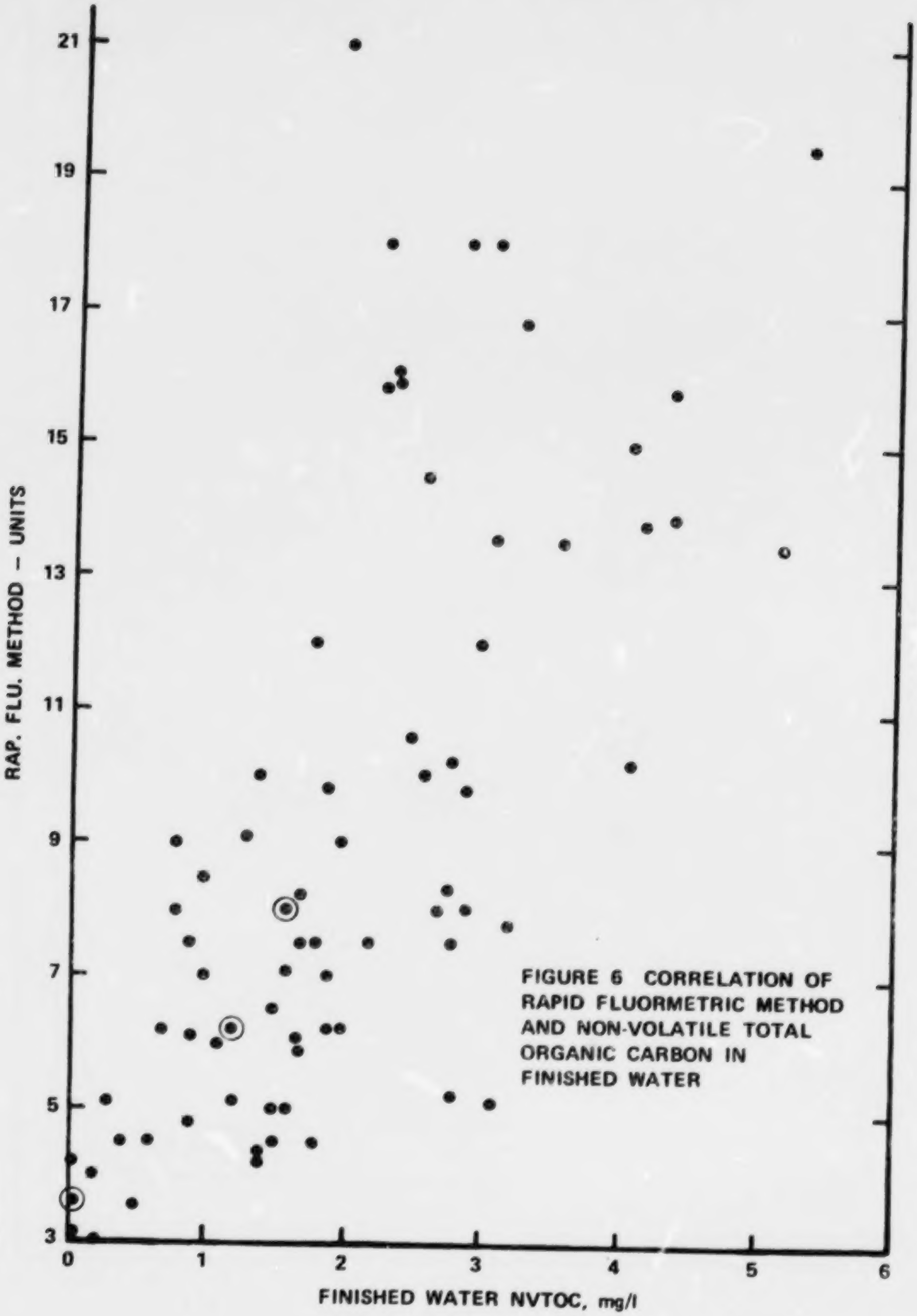

FIGURE 6 CORRELATION OF RAPID FLUORMETRIC METHOD AND NON-VOLATILE TOTAL ORGANIC CARBON IN FINISHED WATER

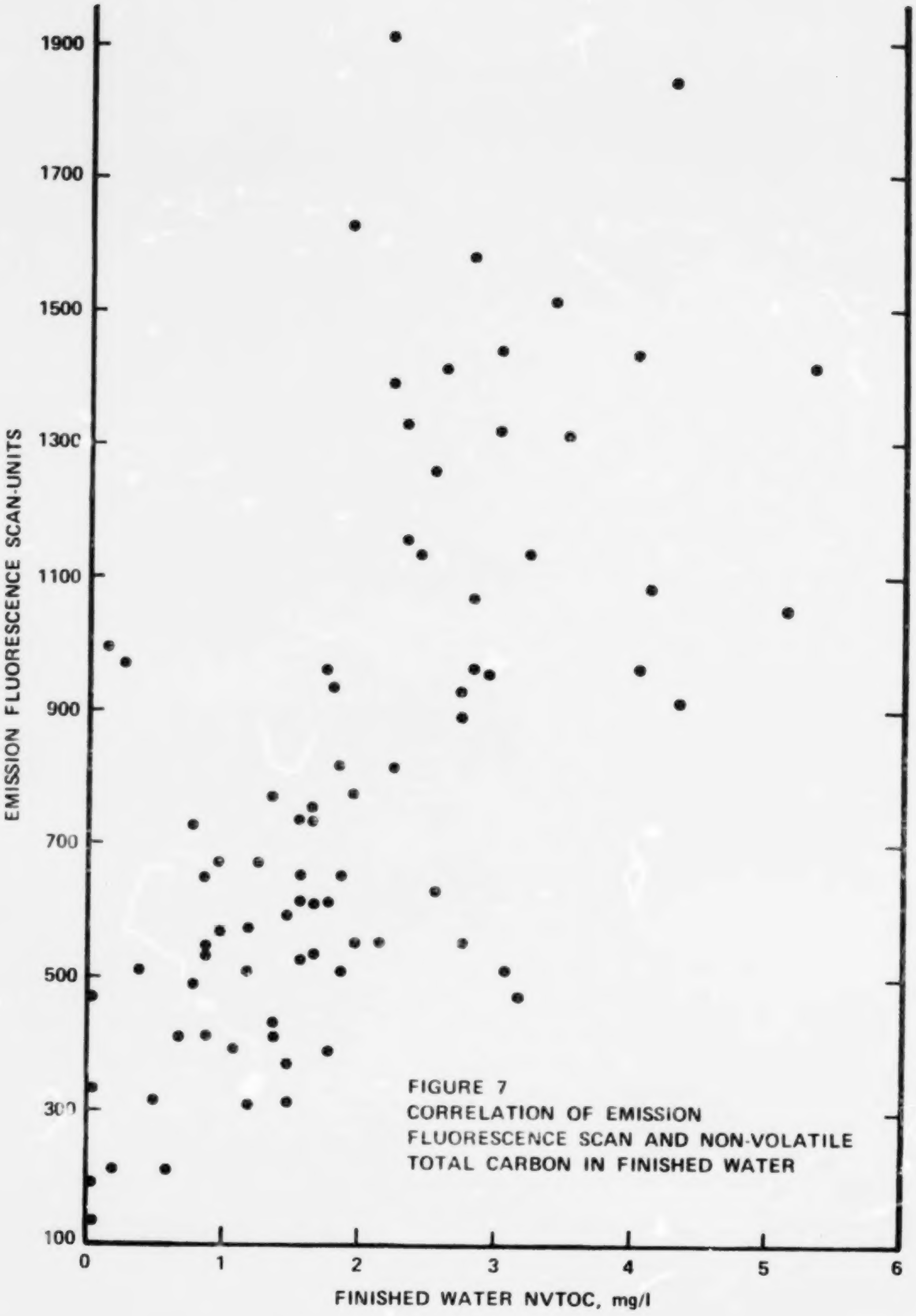

FIGURE 7
CORRELATION OF EMISSION FLUORESCENCE SCAN AND NON-VOLATILE TOTAL CARBON IN FINISHED WATER

F. ACKNOWLEDGMENTS

The following organizational units of EPA contributed to the timely conduct of the National Organics Reconnaissance Survey and to the preparation of this report.

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- Southeast Environmental Research Laboratory, ORD
- R. S. Kerr Environmental Research Laboratory, ORD
- Office of Environmental Sciences, ORD
- Office of Monitoring Systems, ORD
- National Field Investigations Center - Cincinnati, OE
- Water Supply Division, OWHM
- Regional Water Supply Representatives

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Special commendation is due Mrs. Maura M. Lilly who typed the entire first draft of this appendix in three working days.

G. REFERENCES

1. Buelow, R. W., J. K. Carswell and J. M. Symons, "An Improved Method for Determining Organics by Activated Carbon Adsorption and Solvent Extraction (Parts I and II)," Journal American Water Works Association, 65, 57-72, 195-199 (Jan.-March 1973).

2. Bellar, T. A. and J. J. Lichtenberg, "The Determination of Volatile Organic Compounds at the μg/l Level in Water by Gas Chromatography," USEPA Report, NERC, Cincinnati, EPA-670/4-74-009, Nov. 1974.

3. Stevens, A. A. and J. M. Symons, "Analytical Considerations for Halogenated Organic Removal Studies," USEPA Water Supply Research Laboratory, NERC-Cincinnati, Dec. 1974, Prepublication copy.

4. "Method for Polychlorinated Biphenyls in Industrial Effluents," National Pollution Discharge Elimination System, Appendix A, Methods Development and Quality Assurance Research Laboratory, Cincinnati, Ohio, November 28, 1973.

5. Dressman, R. C. and E. F. McFarren, "Detection and Measurement of Bis-(2-chloro) Ethers and Dieldrin by Gas Chromatography," Second Annual Water Quality Conference of American Water Works Association, Dallas, Texas, December 2-4, 1974.

6. Bellar, T. A. and J. J. Lichtenberg, "Determining Volatile Organics at the μg/l Level in Water by Gas Chromatography," JAWWA, 66, 739-744 (December 1974).

7. "Method for Organophosphorous Pesticides in Industrial Effluents," National Pollution Discharge Elimination System, Appendix A, Methods Development and Quality Assurance Research Laboratory, Cincinnati, Ohio, November 28, 1973.

8. Dobbs, R. A., R. H. Wise and R. B. Dean, "The Use of Ultraviolet Absorbance for Monitoring the Total Organic Carbon Content of Water and Wastewater," Water Research, 6, 1173-80 (1972).

9. Sylvia, A., "Detection and Measurement of Microorganics in Drinking Water," Jour. New Eng. Water Works Assn., 87, No. 2 (June 1973).

10. Standard Methods for the Examination of Water and Wastewater, 13th Edition, American Public Health Association, New York, New York.

11. "Methods for Chemical Analysis of Water and Wastewater," U. S. Environmental Protection Agency, 1974.

12. Caldwell, J. S., R. J. Lishka, and E. F. McFarren, "Evaluation of Low-Cost Arsenic and Selenium Determination at Microgram-per-Liter Levels," JAWWA, 63, 731 (1973).

13. "Cyanide in Water and Wastewater, Industrial Method," No. 119-71W, April 1972, Technicon Instrument Corp., Tarrytown, New York.

14. Kopp, J. F., M. C. Longbottom, and L. B. Lobring, "Cold Vapor Method for Determining Mercury," *JAWWA*, *64*, 20 (1972).

15. *Organochlorine Pesticides in Water, 1974 Annual Book of ASTM Standards*, American Society for Testing Materials.

16. Georlitz, D. T., and W. L. Lower, *Determination of Phenoxy Acid Herbicides in Water by Electron Capture and Micro Coulometric Gas Chromatography*, Geological Survey Water Supply Paper 1817C, U. S. Government Printing Office.

17. Rook, J. J., "Formation of Haloforms During Chlorination of Natural Waters," *Water Treatment and Examination*, *23*, Part 2, 234-243 (1974).

18. Bellar, T. A., J. J. Lichtenberg, and R. C. Kroner, "The Occurrence of Organohalides in Chlorinated Drinking Water," *JAWWA*, *66*, 703-706, (December 1974).

APPENDIX III

ORGANIC CHEMICALS FOUND IN INDUSTRIAL EFFLUENTS

Southeast Environmental Research Laboratory
Athens, Georgia

and

Office of Research and Development
Environmental Protection Agency
Washington, D.C.

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ORGANIC CHEMICALS IN INDUSTRIAL EFFLUENTS

The compositions of industrial effluents are being systematically studied at the Southeast Environmental Research Laboratory. In addition, short-term studies for special purposes have been conducted at the request of Regional and other offices. Table 1 is a composite list of substances and their sources as of mid-1973. Compounds in textile mill effluents identified since 1973 are listed in Table 2.

In general the lists of compounds already found in drinking water appear to have more in common with the lists of compounds occurring in industrial wastes than the list of compounds occurring in domestic sewage. Of those substances identified as suspect carcinogens, two, chloroform and bis (2-chloroethyl) ether appear in industrial wastes and have not been shown to occur in domestic sewage. It should be mentioned, however, that there is the possibility that these compounds are formed during the chlorination of drinking water.

With the presently available information, it would appear that the organic substances occurring in drinking water are for the large part of industrial origin. Where special studies have been undertaken to identify specific compounds causing problems, such as taste and odor, in water supplies, the results have led to the conclusion that the causative agents were of industrial origin. It should be kept in mind, however, that the analyses of drinking water, municipal wastewaters and industrial effluents is continuing and the final results may present a somewhat different picture.

Table 1

ORGANIC CHEMICALS FOUND IN INDUSTRIAL WASTES

Compound	Sample source
6,8,11,13-Abietatetraen-18-oic acid	Paper mill's raw waste and trickling filter effluent
13-Abieten-18-oic acid	Paper mill's raw waste and trickling filter effluent
Abietic acid	Paper mill's raw waste and lagoon
Acenaphthalene	Petrochemical plant's five-day lagoon effluent
Acenaphthene	Petrochemical plant's five-day lagoon effluent
"	Wood preserving plant's lagoon effluent
"	Wood preserving plant's settling pond
"	Pesticide plant's raw effluent
Acetophenone	Chlorinated paraffin plant's lagoon
"	Petrochemical plant's five-day lagoon effluent
Acetosyringone	Gulf coast paper mill's settling pond
Acetovanillone	Gulf coast paper mill's settling pond
"	Paper mill's raw waste and lagoon

Table 1 (Continued)

2-Acetylthiophene	Paper mill's raw waste
Acrylonitrile	Acrylic fiber plant's settling pond
Adipic acid	Nylon plant's raw waste
Adiponitrile	Nylon plant's raw waste
Aldrin	Pesticide plant's raw effluent
m-Anethole	Paper mill's raw waste
o-Anethole	Paper mill's raw waste
p-Anethole	Paper mill's raw waste
Anthraquinone	Wood preserving plant's settling pond
Anteisomargaric acid	Paper mill's raw waste and five-day lagoon
Anteisopentadecanoic acid	Paper mill's five-day lagoon
Arachidic acid	Paper mill's raw waste
Arachidonic acid	Paper mill's five-day lagoon
Behenic acid	Paper mill's raw effluent and five-day lagoon
Benzaldehyde	Paper mill's raw waste
Benzyl alcohol	Petrochemical plant's five-day lagoon effluent
2-Benzothiazole	Latex accelerators and thickeners plant's holding pond
"	Synthetic rubber plant's aerated lagoon

Table 1 (Continued)

Biphenyl	River below textile finishing plant
Borneol	Paper mill's raw waste and trickling filter effluent
1-Butanol	Petrochemical (alcohols) plant's raw effluent
2-Butoxyethanol	Petrochemical plant's five-day lagoon effluent
n-Butylisothiocyanate	Latex accelerators and thickeners plant's holding pond
Camphor	Paper mill's raw waste and trickling filter effluent
"	Gulf coast paper mill's settling pond
Caproic acid	Nylon plant's raw waste
Carbazole	Wood preserving plant's settling pond
Chlordane	Pesticide plant's raw effluent
Chlordene	Pesticide plant's raw waste
o-Chlorobenzoic acid	Chlorinated paraffin plant's lagoon
bis-(2-Chloroethoxy) methane	Synthetic rubber plant's treated waste
bis-2-Chloroethyl ether	Synthetic rubber plant's treated waste
bis-2-Chloroisopropyl ether	Glycol plant's thickening and sedimentation pond
trans-Communic acid	Paper mill's raw waste and trickling filter effluent

Table 1 (Continued)

o-Cresol	Wood preserving plant's settling pond
o-Cresol	Petrorefinery's eight-hour lagoon effluent
m-Cresol	Wood preserving plant's settling pond
p-Cresol	Paper mill's raw waste and lagoon
Cumene (isopropylbenzene)	Petrochemical plant's five-day lagoon effluent
Cyclohexanol	Nylon plant's raw waste
1,5-Cyclooctadiene	Petrochemical plant's five-day lagoon effluent
p-Cymene	Paper mill's raw waste and trickling filter effluent
"	Pesticide plant's raw waste
Decane	Polyolefin plant's lagoon
1-Decanol	Petrochemical (alcohols) plant's raw effluent
Dehydroabietic acid	Wood preserving plant's settling pond
"	Paper mill's raw waste and trickling filter effluent
"	Gulf coast paper mill's settling pond
"	Tall oil refinery's settling pond
Diacetone alcohol	Petrochemical plant's five-day lagoon effluent

Table 1 (Continued)

4,4'-Diamino-dicyclohexyl methane	Nylon and polyester plant's effluent after neutralization and sedimentation
Dibenzofuran	Wood preserving plant's settling pond
"	Wood preserving plant's lagoon effluent
"	Nylon plant's settling pond
2,3-Dibromo-1-propanol	Acrylic fibers plant's settling pond
Dibromopropene isomer	Acrylic fibers plant's settling pond
Dibutylamine	Latex accelerators and thickeners plant's raw effluent
Dieldrin	Anaerobic lagoon of yarn finishing mill
"	Pesticide plant's raw effluent
N,N-Diethylformamide	Latex accelerators and thickeners plant's raw effluent
Diethyl phthalate	Synthetic rubber plant's settling pond
3,4-Dihydroxyacetophenone (pungenin)	Paper mill's trickling filter effluent
3,5-Dimethoxy-4-hydroxy-acetophenone	Paper mill's raw effluent and five-day lagoon
2,4-Dimethyldiphenylsulfone	Nylon plant's settling pond
"	Acrylic fibers plant's settling pond

Table 1 (Continued)

Dimethyl furan isomer	Petrochemical plant's five-day lagoon effluent
2,6-Dimethyl naphthalene	Petrochemical plant's five-day lagoon effluent
Dimethyl naphthalene isomer	Pesticide plant's raw effluent
Dimethyl phthalate	Plastic (PVA) plant's settling pond
"	Synthetic rubber plant's settling pond
Dimethyl pyridine isomer	Wood preserving plant's settling pond
Dimethyl quinoline isomers	Wood preserving plant's settling pond
Dimethyl sulfone	Paper mill's raw waste and trickling filter effluent
Dimethyl sulfoxide	Paper mill's raw waste and trickling filter effluent
10,12-Dimethyl tridecanoic acid	Paper mill's five-day lagoon
4,6-Dinitro-o-cresol (2-methyl-4,6-dinitro-phenol)	Specialty chemical plant's effluent
2,4-Dinitrotoluene	Explosives (DNT) plant's raw waste and settling pond effluent
2,6-Dinitrotoluene	Explosives (DNT) plant's raw waste and settling pond effluent
"	TNT plant's raw effluent
3,4-Dinitrotoluene	Explosives (DNT) plant's raw waste and settling pond effluent

Table 1 (Continued)

Diphenylene sulfide	Wood preserving plant's settling pond
Diphenyl ether	Pesticide plant's raw effluent
3,3-Diphenylpropanol	Petrochemical plant's five-day lagoon effluent
2,6-Di-t-butyl-p-benzo-quinone	Surface drainage from closed waste treatment system of particle board plant
p-Dithiane	Synthetic rubber plant's treated waste
Dodecane	Petrorefinery's lagoon effluent after activated sludge treatment
"	Petrorefinery's eight-hour lagoon effluent
"	Paper mill's raw effluent
Eicosane (C_{20})	Petrorefinery's lagoon effluent after activated sludge treatment
Endrin	Pesticide plant's raw effluent
Ethyl carbamate	Paper mill's trickling filter and aerated lagoon
2-Ethyl-1-hexanol	Gulf coast paper mill's settling pond
"	Laboratory sewage
"	Plastic (PVA) plant's settling pond
"	River below textile finishing plant
Ethylidenecyclopentane	Paper mill's raw waste

Table 1 (Continued)

Ethyl isothiocyanate	Latex accelerators & thickeners plant's raw effluent
Ethyl naphthalene isomer	Petrochemical plant's five-day lagoon effluent
"	Pesticide plant's raw effluent
m-Ethyl phenol	Paper mill's raw waste and lagoon
Ethyl phenylacetate	Resin plant's lime treated holding pond effluent
o-Ethyl toluene	Petrochemical plant's five-day lagoon effluent
Eugenol	Paper mill's raw waste and lagoon
Fenchyl alcohol	Paper mill's raw waste and trickling filter effluent
Fenchone	Paper mill's raw waste and trickling filter effluent
Fluoranthene	Wood preserving plant's settling pond
Fluorene	Wood preserving plant's settling pond
"	Petrochemical plant's five-day lagoon effluent
2-Formylthiophene	Paper mill's raw waste
Furfural	Paper mill's raw waste
"	Synthetic rubber plant's settling pond
Guaiacol	Gulf coast paper mill's settling pond

Table 1 (Continued)

Guaiacol	Paper mill's raw waste and trickling filter effluent
Heneicosane (C_{21})	Petrorefinery's lagoon effluent after activated sludge treatment
Heptachlor	Pesticide plant's raw waste
Heptachloronorbornene isomers	Pesticide plant's raw effluent
Heptadecane	Nylon plant's settling pond
"	Petrorefinery's eight-hour lagoon effluent
"	Petrorefinery's lagoon effluent after activated sludge treatment
Hexachlor epoxide	Pesticide plant's raw waste
Hexachlorobenzene	Chlorinated solvents plant's raw effluent
Hexachlorobutadiene	Pesticide plant's raw effluent
Hexachlorocyclopentadiene	Pesticide plant's raw waste
Hexachloronorbornadiene isomers	Pesticide plant's raw effluent
Hexadecane	Nylon plant's settling pond
"	Petrorefinery's eight-hour lagoon effluent
"	Petrorefinery's lagoon effluent after activated sludge treatment
"	Paper mill's raw waste

Table 1 (Continued)

Hexadecane	Petrochemical plant's five-day lagoon effluent
Hexadieneal	Pesticide plant's raw effluent
1-Hexanol	Petrochemical (alcohols) plant's raw effluent
Homovanillic acid	Paper mill's raw waste and five-day lagoon
p-Hydroxyacetophenone	Paper mill's raw waste and lagoon
p-Hydroxybenzaldehyde	Paper mill's raw waste and lagoon
o-Hydroxybenzoic acid	Paper mill's raw waste
Hydroxybiphenyl isomer	Pesticide plant's raw effluent
4-Hydroxy-3 methoxypropiophenone	Paper mill's raw effluent
p-Hydroxythiophenol	Paper mill's raw waste
Indan	Petrochemical plant's five-day lagoon effluent
Indene	Petrochemical plant's five-day lagoon effluent
Isodrin	Pesticide plant's raw effluent
Isoeugenol	Paper mill's raw waste and lagoon
Isopalmitic acid	Paper mill's five-day lagoon
Isopentyl alcohol	Laboratory sewage
Isooctyl phthalate	Nylon plant's raw waste
Isopimaric acid	Paper mill's raw waste and trickling filter effluent

Table 1 (Continued)

Jasmone	Pesticide plant's raw effluent
Lignoceric acid	Paper mill's raw waste
Limonene	Paper mill's raw waste and trickling filter effluent
Linoleic acid	Paper mill's raw waste and lagoon
Mandelic acid	Paper mill's raw waste
Margaric acid	Paper mill's raw waste
2-Mercaptobenzothiazole	Synthetic rubber plant's aerated lagoon
"	Paper mill's raw waste and lagoon
alpha-Methylbenzyl alcohol	Petrochemical plant's five-day lagoon effluent
Methyl biphenyl isomer	Petrochemical plant's five-day lagoon effluent
Methyl 3,4-Dimethoxybenzyl ether	Paper mill's raw waste
2-Methyl-4-ethyl dioxolane	Fiberglass plant's effluent
Methyl ethyl naphthalene isomer	Petrochemical plant's five-day lagoon effluent
1-Methyl indene	Petrochemical plant's five-day lagoon effluent
3-Methyl indene	Petrochemical plant's five-day lagoon effluent
1-Methyl naphthalene	River below textile finishing plant

Table 1 (Continued)

1-Methyl naphthalene	Petrorefinery's eight-hour lagoon effluent
"	Petrochemical plant's five-day lagoon effluent
"	Synthetic rubber plant's settling pond
2-Methyl naphthalene	Petrorefinery's eight-hour lagoon effluent
"	Petrochemical plant's five-day lagoon effluent
Methyl naphthalene isomer	Wood preserving plant's lagoon effluent
Methyl naphthalene isomers	Pesticide plant's raw effluent
13-Methyl pentadecanoic acid	Paper mill's five-day lagoon
Methyl phenanthrene	Wood preserving plant's lagoon effluent
Methyl quinoline isomers	Wood preserving plant's settling pond
o-Methylstyrene	Petrochemical plant's five-day effluent
beta-Methylstyrene	Petrochemical plant's five-day lagoon effluent
Methyl trisulfide	Paper mill's raw waste
Myristic acid	Paper mill's raw waste
Naphthalene	Nylon plant's settling pond
"	Surface drainage from closed treatment of system of particle board plant

Table 1 (Continued)

Naphthalene	Petrochemical plant's five-day lagoon effluent
"	Pesticide plant's raw waste
2-Naphthoic acid	Wood preserving plant's settling pond
Neoabietic acid	Paper mill's raw waste
Nitrobenzene	Chemical company's lagoon after steam stripping
2-Nitro-p-cresol	Chemical company's lagoon after steam stripping
o-Nitrophenol	Chemical company's lagoon after steam stripping
o-Nitrotoluene	Paper mill's five-day lagoon
"	TNT plant's raw effluent
"	DNT plant's raw effluent
m-Nitrotoluene	DNT plant's raw effluent
p-Nitrotoluene	Chemical company's lagoon after steam stripping
"	DNT plant's raw effluent
Nonachlor	Pesticide plant's raw effluent
Nonadecane	Petrorefinery's lagoon effluent after activated sludge treatment
"	Petrorefinery's eight-hour lagoon effluent
Nonylphenol	Anaerobic lagoon of yarn finishing mill

Table 1 (Continued)

Nonylphenol	River below textile finishing plant
Norcamphor	Paper mill's raw waste
beta-Ocimene	Paper mill's raw waste
1-Octanol	Petrochemical (alcohols) plant's raw effluent
Octachlorocyclopentene	Pesticide plant's raw effluent
Octadecane	Petrorefinery's eight-hour lagoon effluent
"	Nylon plant's settling pond
Oleic acid	Tall oil refinery's settling pond
"	Paper mill's raw waste and trickling filter effluent
Octylphenol	River below textile finishing plant
Palmitic acid	Textile chemical plant's raw effluent
"	Tall oil refinery's settling pond
"	Paper mill's raw waste and trickling filter effluent
"	Gulf coast paper mill's settling pond
Palmitoleic acid	Paper mill's five-day lagoon
Pentachlorocyclopentadiene isomers	Pesticide plant's raw effluent
Pentachloronorbornadiene isomer	Pesticide plant's raw effluent

Table 1 (Continued)

Pentachloronorbornene isomer	Pesticide plant's raw effluent
"	Pesticide plant's raw waste
Pentachloronorbornadiene epoxide isomer	Pesticide plant's raw waste
Pentachlorophenol	Latex accelerators and thickeners plant's holding pond
"	Wood preserving plant's raw effluent
"	Resin plant's lime treated holding pond effluent
"	Synthetic rubber plant's aerated lagoon
"	Wood preserving plant's lagoon effluent
Pentadecane	Petrorefinery's eight-hour lagoon effluent
"	Petrorefinery's lagoon effluent after activated sludge treatment
"	Paper mill's raw waste
"	Petrochemical plant's five-day lagoon effluent
Pentadecanoic acid	Paper mill's lagoon
Phenanthrene	Wood preserving plant's lagoon effluent
"	Wood preserving plant's settling pond
Phenol	Laboratory sewage

Table 1 (Continued)

Phenol	Petrorefinery's eight-hour lagoon effluent
"	Wood preserving plant's settling pond
"	Petrochemical plant's five-day lagoon effluent
"	Paper mill's raw waste
Phenyl ether	Nylon plant's settling pond
o-Phenylphenol	River below textile finishing plant
Pimaric acid	Paper mill's raw waste and trickling filter effluent
"	Gulf coast paper mill's settling pond
beta-Pinene	Paper mill's raw waste
Pinene isomer	Gulf coast paper mill's settling pond
Polychlorinated biphenyls (Arochlor 1254)	Nylon plant's raw waste
2-Propionylthiophene	Paper mill's raw waste
4-n-Propylphenol	Paper mill's raw waste and lagoon
Pyrene	Wood preserving plant's settling pond
Quinoline	Wood preserving plant's settling pond
Sandaracopimeric acid	Paper mill's raw waste and lagoon

Table 1 (Continued)

Stearic acid	Textile chemical plant's raw effluent
"	Gulf coast paper mill's settling pond
Styrene	Petrochemical plant's five-day lagoon effluent
"	Synthetic rubber plant's settling pond
Syringaldehyde	Gulf coast paper mill's settling pond
"	Paper mill's lagoon
Terpinene-4-ol	Paper mill's raw waste
alpha-Terpineol	Nylon plant's settling pond
"	Paper mill's raw waste and trickling filter effluent
"	Petrochemical plant's five-day lagoon effluent
Terpineol isomer	Gulf coast paper mill's settling pond
Terpinolene	Paper mill's raw waste
1,1,2,2-Tetrachloroethane	Chlorinated solvents plant's raw effluent
Tetrachlorophenol isomer	Wood preserving plant's raw effluent
Tetradecane	Petrorefinery's lagoon effluent after activated sludge treatment
"	Petrorefinery's eight-hour lagoon effluent

Table 1 (Continued)

Tetramethylbenzene isomer	Pesticide plant's raw waste
2,2'-Thiodiethanol (Thiodiglycol)	Synthetic rubber plant's treated waste
Toluic acid	Chlorinated paraffin plant's lagoon
Trichlorobenzene isomer	River below textile finishing plant
"	Textile chemical plant's raw effluent
Trichlorocyclopentene isomers	Pesticide plant's raw effluent
1,1,2-Trichloroethane	Chlorinated solvents plant's raw effluent
Trichloroguaiacol	Paper mill's raw waste
n-Tridecane	Petrorefinery's eight-hour lagoon effluent
"	Petrorefinery's lagoon effluent after activated sludge treatment
"	Paper mill's raw waste
Triethylurea	Latex accelerators & thickeners plant's raw effluent
3,4,5-Trimethoxyacetophenone	Paper mill's raw waste and trickling filter effluent
2,4,6-Trimethylpyridine	Wood preserving plant's settling pond
2,4,6-Trinitrotoluene	TNT plant's raw effluent
n-Undecane	Paper mill's raw waste

Table 1 (Continued)

n-Undecane	Petrorefinery's eight-hour lagoon effluent
"	Polyolefin plant's lagoon
"	Petrorefinery's lagoon effluent after activated sludge treatment
Valeric acid	Nylon plant's raw waste
Vanillin	Paper mill's raw waste and trickling filter effluent
"	Gulf coast paper mill's settling pond
Veratraldehyde	Paper mill's raw waste & lagoon
o-Xylene	Syntehtic resin plant's settling pond
"	Petrochemical plant's five-day lagoon effluent
m-Xylene	Petrochemical plant's five-day lagoon effluent
p-Xylene	Petrochemical plant's five-day lagoon effluent
2,5-Xylenol	Wood preserving plant's settling pond
3,4-Xylenol	Wood preserving plant's settling pond
3,5-Xylenol	Wood preserving plant's settling pond

Table 2

ORGANIC COMPOUNDS IN TEXTILE EFFLUENTS

Compound
1,2,4-trichlorobenzene
benzoic acid (methyl ester)
p-nonylphenol
p-tert -butylphenol
di-n-butyl phthalate
methyl isobutyl ketone
acetophenone
chlorobenzene
p-dichlorobenzene
toluene
ethylbenzene
naphthalene
1-methylnaphthalene
dodecane
2-methylpyrrolidone
1,3,5-trimethylbenzene
cymene
tridecane
tetradecane
chloroform
tetrachloroethylene
styrene
o-phenylphenol
biphenyl
diphenyl oxide
ethylene dichloride
benzophenone
n-butanol

MONITORING FOR RADIATION IN DRINKING WATER

This appendix focuses on the Environmental Radiation Ambient Monitoring System. Radium-226 and methods of removing it from water supplies are the subject of section C(4) of Appendix VI.

The Environmental Radiation Ambient Monitoring System (ERAMS), which began in July 1973, was developed from previously operating radiation monitoring networks to form a single monitoring system more responsive to current and projected sources of environmental radiation.

The ERAMS Drinking Water Component is an expansion of the previous Tritium Surveillance System which was operated by the Office of Radiation Programs from 1970 through June 1973. The Drinking Water Component consists of 77 quarterly drinking water samples taken from major population centers and selected nuclear facility environs. Tritium is analyzed on a quarterly basis with grab samples. Tritium, a long-lived (half-life of 12.3 years) isotope of hydrogen (hydrogen-3), is produced in nuclear power production and nuclear weapons testing, and naturally by cosmic radiation. Because it is chemically similar to hydrogen, tritium readily enters the body as water and is incorporated into living tissue.

Table 1 presents the tritium concentrations in drinking water at the Drinking Water Component stations for 1974. The average tritium concentration was 0.3 nCi/liter. The radiation dose to individuals may be calculated from the formula:

$$H \text{ (mrem/year)} = 0.1C \text{ (nCi/liter)}$$

where H is the dose equivalent rate and C represents the tritium concentration in body water in nCi/liter (nCi = 10^{-9} curie). Assuming that the concentration of tritium in all water taken into the body is equal to that found in the drinking water, and that the specific activity of tritium in the body is essentially the same as that in the drinking water, then the radiation dose to individuals may be estimated. The highest individual concentration of tritium observed in drinking water was 6.8 nCi/liter during 1974. This corresponds to a dose of 0.7 mrem/year (0.007 rem/year). The average tritium concentration during 1974 was 0.3 mrem/year. The calculated health effects to the U. S. population may be estimated by using a risk factor of 7×10^{-4} health effects per person-rem. Therefore, the calculated number of potential health effects in the U. S. population would be 4.5 based upon a constant intake at the average concentration.

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Table 1

ERAMS Drinking Water Component, 1974

Location	Tritium concentration[a] (nCi/liter ± 2σ)[b]			
	Jan-Mar	April-June	July-Sept	Oct-Dec
Ala: Dothan----------	0	0	0	0
Montgomery------	0	.2	0	0
Muscle Shoals---	0	.3	.3	.2
Alaska: Anchorage-------	NS	0	.5	.4
Fairbanks-------	.5	.5	.5	.3
Ark: Little Rock-----	0	0	0	0
Calif: Berkeley--------	.2	.2	.2	0
Los Angeles-----	0	0	0	0
C. Z: Ancon-----------	.5	0	0	0
Colo: Denver----------	.5	.5	.4	.6
Platteville-----	.9	1.0	.9	.6
Conn: Hartford--------	0	0	.2	.2
Del: Wilmington------	.3	0	.3	.3
D. C: Washington------	0	.2	0	0
Fla: Miami-----------	0	0	0	0
Tampa-----------	0	0	0	0
Ga: Baxley----------	NS	0	NS	0
Savannah--------	3.1 ± 0.3	6.8 ± 0.3	3.0	2.9
Hawaii: Honolulu--------	0	0	0	0
Idaho: Boise-----------	.3	0	NS	.2

Table 1 (Continued)

Location		Tritium concentration[a] (nCi/liter ± 2σ)[b]			
		Jan-Mar	April-June	July-Sept	Oct-Dec
Idaho:	Idaho Falls----	.3	.3	.6	.3
Ill:	Chicago--------	1.0	.6	0	.2
	Morris---------	0	0	0	0
Iowa:	Cedar Rapids---	NS	NS	.3	.5
Kans:	Topeka---------	0	0	.3	0
La:	New Orleans----	.2	0	.3	.3
Maine:	Augusta--------	.2	0	0	.2
Md:	Baltimore------	0	NS	.3	.5
	Conowingo------	0	0	.3	.3
Mass:	Lawrence-------	0	.2	.2	0
	Rowe-----------	.3	0	NS	.[illegible]
Mich:	Detroit--------	.4	.4	.4	.2
	Grand Rapids---	.3	0	.3	.2
Minn:	Minneapolis----	.4	.3	.5	.5
	Red Wing-------	0	0	0	0
Miss:	Jackson--------	0	0	0	.2
Mo:	Jefferson City-	0	.4	0	0
Mont:	Helena---------	.3	.5	.4	.4
Nebr:	Lincoln--------	.2	.2	.2	0
Nev:	Las Vegas------	.8	.7	.6	.7
N. H:	Concord--------	0	.2	.2	.3
N. J:	Trenton--------	0	NS	.2	0

Table 1 (Continued)

Location		Tritium concentration[a] (nCi/liter ± 2σ)[b]			
		Jan-Mar	April-June	July-Sept	Oct-Dec
N. J:	Waretown-------	0	NS	0	0
N. Mex:	Santa Fe-------	.5	NS	.5	0
N. Y:	Albany---------	0	.3	0	.3
	Buffalo--------	.3	.2	.2	.5
	New York-------	.3	NS	.3	0
	Syracuse-------	.6	.6	.5	.7
N. C:	Charlotte------	0	.7	.3	.2
	Wilmington-----	0	0	.2	.2
N. Dak:	Bismarck-------	.5	.5	.7	.4
Ohio:	Cincinnati-----	0	.3	.2	.2
	East Liverpool-	.4	.3	.4	.3
	Painesville----	0	.3	.3	.5
	Toledo---------	NS	NS	NS	NS
Okla:	Oklahoma City--	0	0	.2	0
Oreg:	Portland-------	0	0	0	.3
Pa:	Columbia-------	0	0	.2	.7
	Harrisburg-----	0	.2	.3	.3
	Pittsburg------	.4	.2	.3	.3
P.R:	San Juan-------	0	0	0	0
R.I.:	Providence-----	.2	0	0	0
S.C.:	Anderson-------	.3	.2	.3	.4
	Columbia-------	0	0	.4	.3

Table 1 (Continued)

Location		Tritium concentration[a] (nCi/liter ± 2σ)[b]			
		Jan-Mar	April-June	July-Sept	Oct-Dec
S. C.:	Hartsville-----	0	0	0	0
	Seneca---------	.2	.4	.3	.3
Tenn:	Chattanooga----	.5	.6	.4	0
	Knoxville------	.4	.4	0	0
Tex:	Austin---------	0	0	0	0
Va:	Doswell--------	0	0	0	.2
	Lynchburg------	0	.2	.2	.2
	Norfolk--------	.2	0	0	.2
Wash:	Richland-------	NS	.5	.4	.5
	Seattle--------	.2	0	0	.4
Wisc:	Genoa----------	0	0	NS	0
	Madison--------	0	0	0	0
Average		0.2	0.3	0.3	0.2

[a] The minimum detection limit for all samples was 0.20 nCi/liter. All values equal to or less than 0.20 nCi/liter before rounding have been reported as zero.

[b] The 2σ error for all samples is 0.20 nCi/liter unless otherwise noted.

NS, no sample.

APPENDIX V

ANALYSIS OF INORGANIC CHEMICALS IN WATER SUPPLIES

Table of Contents

Page

A. Interstate Carrier Water Supplies 131

B. Community Water Supply Survey 131

C. Special Studies 131

D. National Organic Reconnaissance Survey Sampling 132

E. Asbestos Studies 135

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ANALYSIS OF INORGANIC CHEMICALS IN WATER SUPPLIES

A. INTERSTATE CARRIER WATER SUPPLIES

For many years the federal government has exercised a regulatory function over the water supplies that provide the water to the watering points of carriers in interstate commerce. If water is loaded aboard a train, ship, plane, or bus, the regulation of the actual watering point is conducted by the Food and Drug Administration, but the regulation of the water systems that supply the water is done by the Environmental Protection Agency.

For these interstate carrier supplies, the state agency controlling community water supplies makes an annual report on the quality of each supply. Besides the summary on the numerous bacteriological samples, data are provided from the most recent chemical analyses on the constituents limited by the Drinking Water Standards. At about three-year intervals, a joint survey is made by the state agency and the EPA Regional Office of each of these 700 or so supplies. At the time of the joint survey, a water sample is collected and sent to the Water Supply Research Laboratory in Cincinnati for analyses of the chemicals limited by the standards.

Tabulation of these data is made periodically, the latest being Chemical Analyses of Interstate Carrier Water Supply Systems, October 1973.[4] Table II is the summary from this report.

B. COMMUNITY WATER SUPPLY SURVEY

Water samples are collected at the water plant for chemical analyses in the interstate state carrier surveillance and by most state agencies. Evidence has been developed that for some constituents the water quality is degraded in distribution. This has been recognized for bacteriological sampling but the effect of the distribution system and household plumbing was not determined by the chemical sampling. The first comprehensive set of data on water quality at the consumer's tap was reported in 1970.[1] A comparison of the results of this study with the 1962 Drinking Water Standards and the American Water Works Association's water quality goals are shown in Table I.

C. SPECIAL STUDIES

EPA has conducted some studies in water systems where the water is particularly corrosive to the distribution system and plumbing. Results of two of these studies have been reported[2] and indicate that a significant number of homes have lead concentrations exceeding the limits. This is most noticeable in the first water drawn in the morning. Human body burden studies are being conducted to see if these high morning concentrations may lead to a health effect. Table III presents some of the water data.

A cooperative study now underway will obtain data on the inorganic chemical content of drinking water at a representative set of homes in the U. S. Water samples are being collected at the homes of persons included in the current series of the National Health Examination Survey. Because of the interest of the National Heart and Lung Institute and EPA in the suggested association of heart disease mortality and soft drinking water, this detailed analysis of drinking water quality and health examination results is underway. The study is designed for health effects research but it will also provide data on water quality for the chemicals limited by the drinking water standards as well as 86 additional chemicals for which we have little information on occurrence in drinking water.

D. NATIONAL ORGANICS RECONNAISSANCE SURVEY SAMPLING

To round out the analyses of NORS and to possibly provide some insight to causes for the developing of the chlorine reaction products, samples were analyzed for the inorganic chemicals proposed to be limited by the new drinking water standards. The results of these analyses are tabulated in Appendix II. Analyses have been completed in all but three of the water systems included in NORS. The results were as expected from previous surveys but because samples were collected at the water plant or well head the pickup of metals in distribution would not be noted. Three supplies exceeded the flouride limits which is comparable with the results of the Community Water Supply Study.[1]

The three samples exceeding the fluoride limit were collected from water supplies adding fluoride in an attempt to provide an optimum concentration. A larger study of 286 water systems in Wisconsin that fluoridated was conducted in 1968-1970.[3] The findings from this study showed that only 40% of the systems that consistently fluoridated produced a water with a fluoride concentration within the range specified in the drinking water standards. These data show that additional surveillance and operator training in methods of good fluoridation practice may be necessary on a national scale.

The one sample exceeding the lead limit was collected from the Huntington, West Virginia, water supply. In any large set of water samples at least one percent exceeds the lead limit which reflects the use of lead pipe and solder for copper pipes. Lead would be of concern if it were consistently over the limit at a sampling point.

Two supplies exceeded the new mercury limit, the Artesian Water Company of New Castle County, Delaware, and the Tennessee American Water Company of Chattanooga. Mercury was detected at the Chattanooga Supply in 1970 also but at half the concentration found in this survey. The Artesian Water Company uses wells and lower mercury concentrations were found in the past.

Table I

Community Water Supply Study

2595 DISTRIBUTION SAMPLES

FROM 969 PUBLIC WATER SUPPLY SYSTEMS

	Recommended Standards			AWWA Goals	
	Limit mg/l	Maximum Concentration	Percent Exceeding	Goal mg/l	Percent Exceeding
A. B. S.	.05	.41	0.0	.20	.2
Arsenic	.01	.10	.4	PHS	.4
Boron	1.0	3.28	.8	PHS	.8
Chloride	250.0	1950.0	1.2	---	---
Color	15.un	49.0	.7	3.un	9.9
Copper	1.0	8.35	1.6	.2	15.5
CCE*	.2	.56	1.2	.04	25.5
Cyanide	.01	.008	0.0	PHS	0.0
Fluoride	Varies	4.40	4.6	PHS	4.6
Iron	0.3	26.0	8.6	.05	44.5
Manganese	0.05	1.32	8.2	.01	31.0
Nitrates	45.0	127.0	2.1	PHS	2.1
Ra-226	3 pCi/l	135.9	.6	PHS	.6
Sr-90	10 pCi/l	2.0	0.0	PHS	0.0
Sulfate	250.0	770.0	1.8	---	---
Dissolved Solids	500.0	2760.0	8.5	200.0	48.7
Turbidity	1-5.un	53.0	2.4	0.1	90.6
Zinc	5.0	13.0	.3	1.0	4.4
CAE*	---	.81	---	.10	26.6
	Mandatory Standards			AWWA Goals	
Arsenic	.05	.10	.2	PHS	.2
Barium*	1.0	1.55	.1	PHS	.1
Boron	5.0	3.28	0.0	PHS	0.0
Cadmium	.01	.011	.2	PHS	.2
Chromium	.05	.08	.2	PHS	.2
Coliforms	1/100 ml.	TNTC	8.8	0.0	11.7
Cyanide	0.2	.008	0.0	PHS	0.0
Fluoride	Varies	4.40	2.1	PHS	2.1
Gross Beta	1000 pCi/l	154.0	0.0	100 pCi/l	<.1
Lead	.05	.64	1.4	PHS	1.4
Selenium	.01	.07	.4	PHS	.4
Silver	.05	.026	0.0	PHS	0.0

*These constituents were evaluated only on selected samples. The remainder were assumed not to exceed the limits or goals.

TABLE II

EXTENT OF NON-COMPLIANCE WITH
1962 USPHS DRINKING WATER STANDARDS

SUBSTANCE	ANALYSES* REPORTED	SAMPLES FAILING DWS RECOMMENDED LIMIT		SAMPLES FAILING DWS MANDATORY LIMIT		SAMPLES WHOSE MINIMUM DETECTABLE LIMIT IS HIGHER THAN THE DWS	
		NO.	%	NO.	%	NO.	%
ABS	282	5	1.8			1	0.4
Arsenic	501						
Barium	405						
Cadmium	541					12	2.2
Chloride	641	17	2.7				
Chromium	535			2	0.4	5	0.9
Copper	555	2	0.4				
CCE	47	6	12.7				
CAE***	19						
Cyanide	237						
Fluoride**	633						
Iron	652	65	10.0			1	0.2
Lead	544			1	0.2	8	1.5
Manganese	623	46	7.4			8	1.3
Mercury***	389			6	1.5	32	8.2
Nitrate	582						
Selenium	344					1	0.3
Silver	411					3	0.7
Sulfate	592	27	4.6				
TDS	575	75	13.0				
Zinc	523	1	0.2				

*Total sampling points - 702
**DWS varies with temperature and not flagged
***Proposed for 1973 Federal Drinking Water Standards

TABLE III

	Percent of Homes with a Sample Exceeding the DWS	
	Boston	Seattle
Cd	0	7%
Cr	0	-
Cu	19%	24%
Fe	9%	76%
Pb	65%	24%
Mn	-	5%
Zn	0	10%

E. ASBESTOS STUDIES

Because of the potential health effect of asbestos fibers in drinking water, the U. S. Environmental Protection Agency has conducted and is currently conducting several studies in an attempt to determine how widespread the problem of asbestos contamination is. This section summarizes the work of EPA's Office of Research and Development and its early findings relative to this issue.

1. Duluth Study

The possibility of asbestos contamination of drinking water at Duluth was discussed by Mrs. Arlene Lehto of Duluth at an International Joint Commission hearing held in Duluth in December 1972. After this, in March 1973 the U. S. EPA National Water Quality Laboratory in Duluth began monitoring the Duluth water supply for amphibole mass by x-ray diffraction. The presence of amphibole fibers was indicated by electron micrographs. This analytical work is continuing. One report was published by Cook et al.[5] They indicated that the total content of amphibole minerals in the Duluth water supply averaged 0.19 mg/l from March 1973 to January 1974.

In June 1973 the U. S. EPA announced that the drinking water of Duluth and North Shore Lake Superior Communities contained asbestiform fibers.

An extensive sampling program was undertaken by Region V in the summer of 1973 in order to learn about the extent of the asbestos contamination problem in Western Lake Superior. Fairless reported on the results of this study.[6] Fairless indicated that in Western Lake Superior, particulate matter from the Silver Bay area was carried by lake currents to the Duluth area and then along the southern shore of the lake (northern Wisconsin and Michigan). The trend for results of both amphibole mass and asbestiform fiber analysis is that the values are lightest at Beaver Bay, Minnesota, decreasing from there to Duluth, and then to Ashland, Wisconsin and Marquette, Michigan.

In 1974 a pilot plant was operated at Duluth's Lakewood Pumping Station for fiber removal research. From May through September Lake Superior water that was pumped into the distribution system at Duluth was analyzed for amphibole mass and asbestiform fibers. Analytical data are shown in Figures 1 and 2. Because of the state of the art in EM analysis for asbestiform fibers in water, a laboratory can be expected to be internally consistent on fiber count from sample to sample, but comparison of results between laboratories is usually not possible. Because no standard method yet exists, some laboratories may count consistently higher than others or vice versa.

Pilot plant results for raw water at the Lakewood Intake (Duluth's drinking water) showed amphibole and chrysotile fiber counts typically in the range of 0.5×10^6 f/l to 2×10^6 f/l, with some samples either higher or lower than that range.

The results of EPA work on waters of western Lake Superior have established firmly the existence of asbestiform fibers. Studies of ways to reduce the fiber content of drinking water are described elsewhere in this report, Appendix VI.

2. Asbestos-Cement Pipe Studies

a. Field Studies

In an effort to study the effect of waters of various corrosiveness on asbestos-cement pipe several systems utilizing A/C pipe were selected for study. In each case, samples were taken of the source and at two places in the distribution system. These will be followed up by analyzing samples from the same locations every month for at least nine months, so as to cover any seasonal variations. Initially three sites were selected. When these are completed or as time permits, others of high pH and hardness will also be selected for study.

b. Controlled Pipe-Loop Study

The objective of this study is to determine the influence of water velocity, aggressiveness of water and elapsed time on the erosion

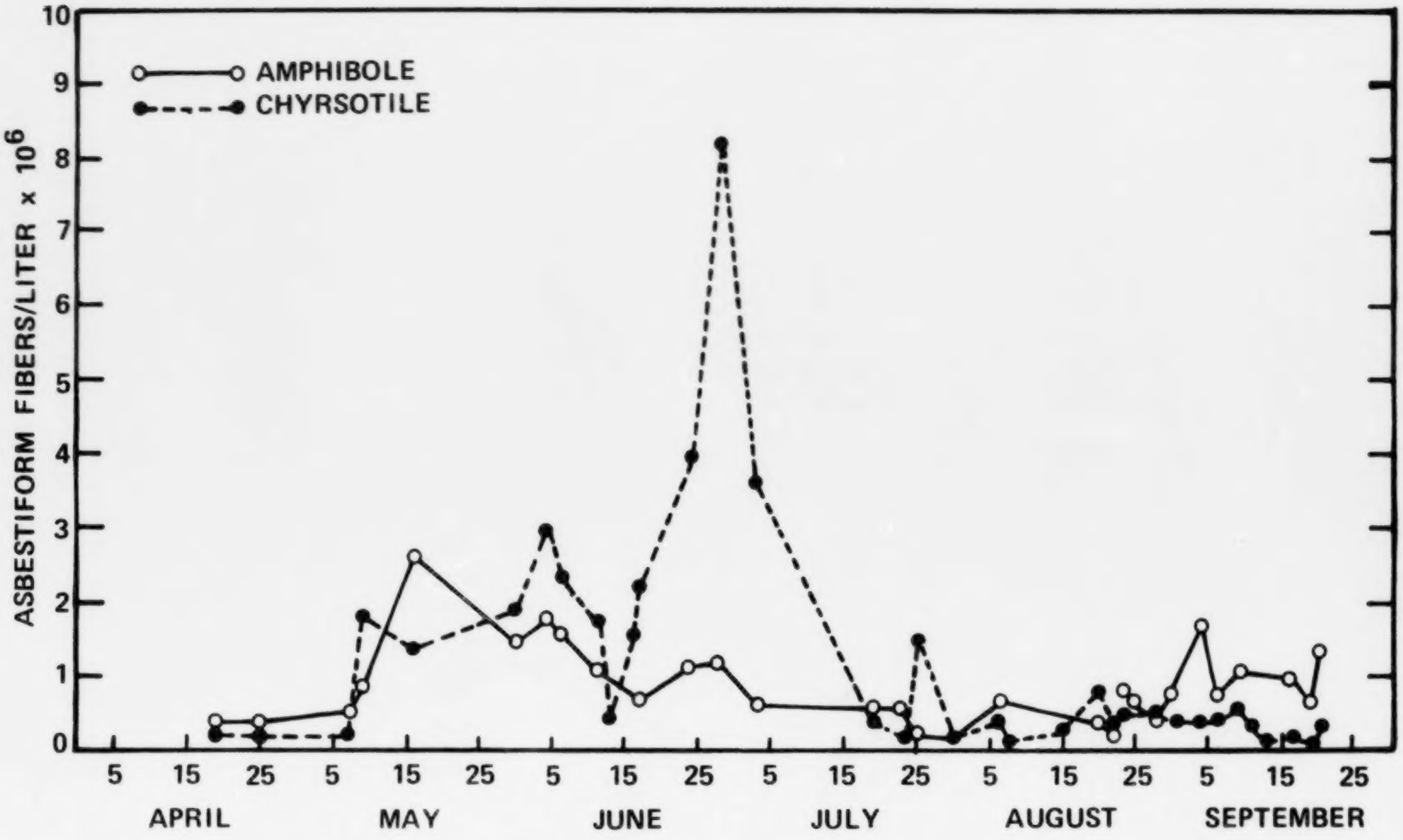

FIGURE 1. ONTARIO RESEARCH FOUNDATION
ASBESTIFORM FIBER COUNTS
RAW WATER AT DULUTH LAKEWOOD INTAKE - 1974

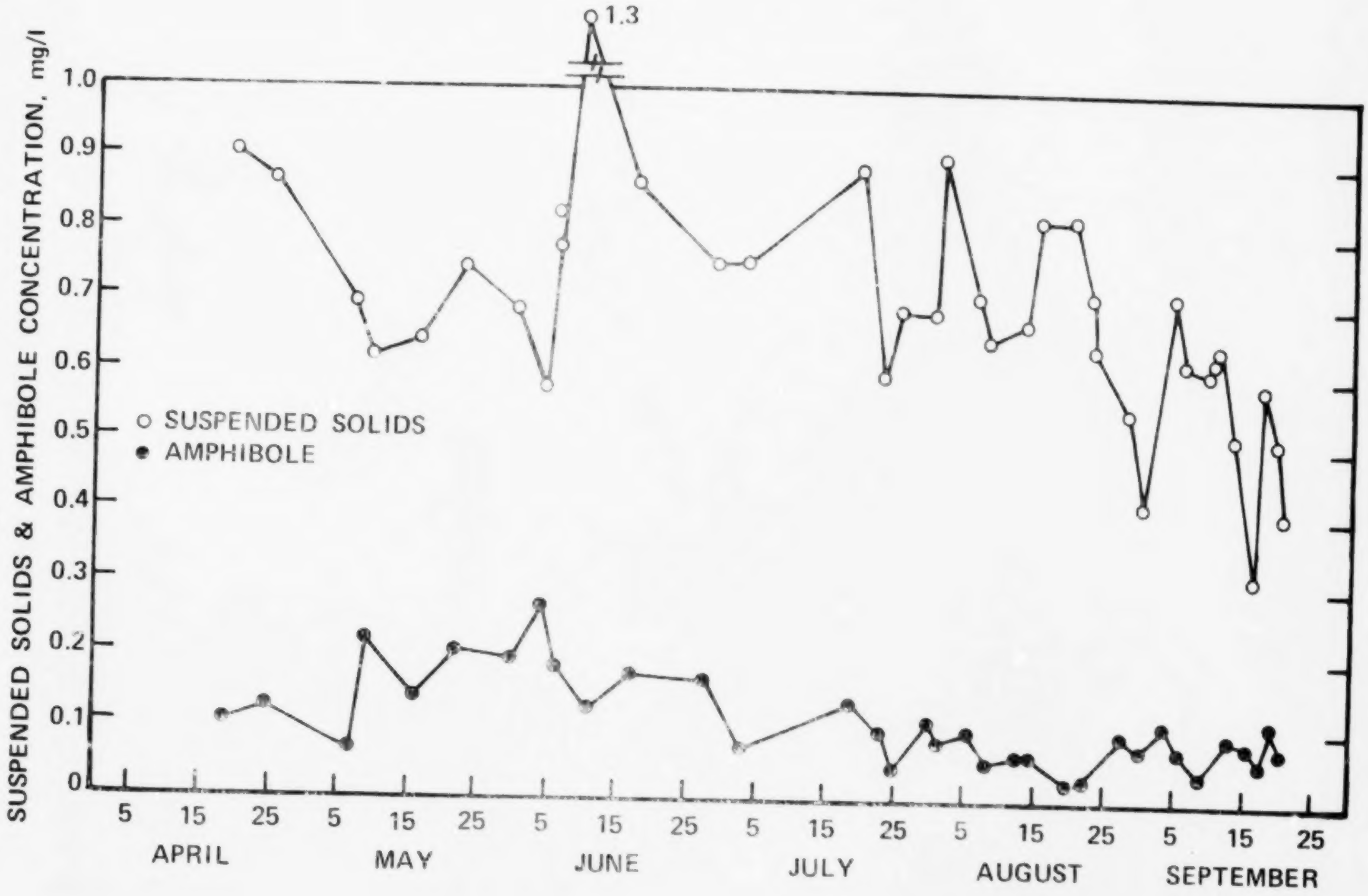

FIGURE 2. ENVIRONMENTAL PROTECTION AGENCY
NATIONAL WATER QUALITY LABORATORY
AMPHIBOLE MASS CONCENTRATION
RAW WATER AT DULUTH LAKEWOOD INTAKE - 1974

of asbestos fibers from asbestos-cement pipe. The influence of tapping the pipe wall will also be studied.

To conduct this study, a "pipe-loop" was constructed of 100 ft of 4-inch and 6-inch diameter asbestos cement pipe. Water is pumped through both pipes at approximately 150 gpm, producing a velocity of 3.8 ft/sec in the 4-inch pipe and 1.7 ft/sec in the 6-inch pipe. As the water entered the pipe test section, it is filtered through a 1 μm pore diameter filter. The pH and hardness of the water are adjusted and maintained at any desired level. Water circulates continuously through the pipe loop. Each day the water passes through an equivalent of 62 miles of 4-inch pipe and 28 miles of 6-inch pipe.

Once each week water is diverted from the exit end of each pipe specimen and 300-500 liters passes through a 0.45 μm pore Millipore filter. Just prior to sampling, water entering the pipe loop is diverted through large 0.45 μm pore Millipore filters to assure that during sampling the water entering the pipe loop is nearly particle-free. Therefore any fibers appearing at the exit end resulted from the test length of pipe. After sampling, the Millipore filters are subjected to EM analysis using the technique cited in Reference 7.

The present plan is to study nine combinations of hardness and pH ranging from a low hardness, low pH water (hardness - 20 mg/l as $CaCO_3$, pH = 5.5) to a high hardness, high pH water (hardness - 400 mg/l as $CaCO_3$, pH = 9.5). Both the hardness and the pH will be varied between the extreme limits in three steps.

The current test involves the use of the low hardness, low pH water. This test has been under way for about two months. Figure 3 shows the results to date. Because of the large volume of water passed through the sampling filters, the test is much more sensitive than the routine analysis for asbestos fibers. This is why such low fiber count can be reported with some degree of reliability.

3. Finished Water at Various Locations in U. S.

In the process of attempting to develop a procedure for the routine analysis of asbestos in water the Water Supply Research Laboratory routinely selected some Interstate Carrier (mostly) Water samples (finished water) received in our laboratory for chemical analysis. The developed procedure has now, or soon will be, published in the Proceedings of the Water Quality Technology Conference, AWWA[7].

The water supplies analysed and the results obtained were as follows:

City	Fibers/l x 10^6
Duluth, Minnesota	1.1 to 4.8 A BDL to 0.4 C
Abilene, Texas	BDL
Cincinnati, Ohio	NSS
Cheyenne, Wyoming	NSS
Columbia, South Carolina	0.13 C
Cairo, Illinois	NSS
Anchorage, Alaska	0.07 A
Jackson, Mississippi (2 grids)	0.25 to 0.7 C
Ashland, Kentucky	BDL
Pittsburgh, California	NSS
N. Troy, Vermont (2 grids)	0.98 to 2.2 C
Enosburg, Vermont	0.05 C
Brattleboro, Vermont	0.11 C
Eden, Vermont (Spring)	0.08 C
St. Louis, Missouri	NSS
Seattle, Washington (Tolt Pipe Line)	1.812 A 2.464 C
Seattle, Washington (Cedar River System)	BDL NSS C
Elizabeth, New Jersey	BDL
Amarillo, Texas	0.09 A
Boulder, Colorado	BDL

City	Fibers/l x 10^6
Glens Falls, New York	BDL
Jonesboro, Arkansas	NSS
New Haven, Connecticut	NSS
Clarksville, Tennessee	0.09 C
Jersey City, New Jersey	0.16 C
Erie, Pennsylvania	0.07 C
Newport, R. I. (2 grids)	0.04 to 1.0 C
Little Rock, Arkansas	0.27 C
Charlottesville, Virginia	NSS
Skidaway Island, Ga. (2 grids)	1.74 to 2.03 C
Jericho - Underhill, Vermont	NSS
Crystal Springs, Vermont	NSS
Niagara Falls, New York	NSS
Rochester, New York	BDL
Buffalo, New York	0.13 C
San Francisco, California	1.54 C
Nashville, Tennessee (2 grids)	0.43 to 0.80 C
South Pittsburgh, Pa.	0.21 C
Independence, Missouri (2 grids)	0.36 to 0.58 C
Montgomery, Ala. (2 grids)	BDL to 0.12 C
Ft. Lauderdale, Florida	NSS
Indianapolis, Indiana	0.18 C
Kansas City, Missouri	0.07 C

City	Fibers/l x 10^6
Springfield, Missouri	0.30 C
Melbourne, Florida	NSS
Tulsa, Oklahoma	BDL
Wilmington. Delaware	0.29 C
Bethlehem, Pa	NSS
Fairbanks, Alaska	BDL
Elmira, New York	NSS
Muskogee, Oklahoma	BDL
Richmond, Harrington, Vt.	NSS
Quarry Hill, Vermont	NSS
Tuscaloosa, Alabama	0.45 C
Birmingham, Alabama	BDL
Topeka, Kansas	NSS
Greenville, S. Carolina	NSS
Yuma, Arizona	0.12 C
Dayton, Ohio	NSS
Washington, D. C.	NSS
Sacramento, California	NSS
Miami, Florida	BDL
San Juan, Puerto Rico	NSS
Chattanooga, Tennessee	0.13 C

BDL - Below detection limit
NSS - Not statistically significant (less than 5 fibers in 20 fields)
A - amphibole
C - chrysotile

City	Fibers/l x 10^6
Glens Falls, New York	BDL
Jonesboro, Arkansas	NSS
New Haven, Connecticut	NSS
Clarksville, Tennessee	0.09 C
Jersey City, New Jersey	0.16 C
Erie, Pennsylvania	0.07 C
Newport, R. I. (2 grids)	0.04 to 1.0 C
Little Rock, Arkansas	0.27 C
Charlottesville, Virginia	NSS
Skidaway Island, Ga. (2 grids)	1.74 to 2.03 C
Jericho - Underhill, Vermont	NSS
Crystal Springs, Vermont	NSS
Niagara Falls, New York	NSS
Rochester, New York	BDL
Buffalo, New York	0.13 C
San Francisco, California	1.54 C
Nashville, Tennessee (2 grids)	0.43 to 0.80 C
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Montgomery, Ala. (2 grids)	BDL to 0.12 C
Ft. Lauderdale, Florida	NSS
Indianapolis, Indiana	0.18 C
Kansas City, Missouri	0.07 C

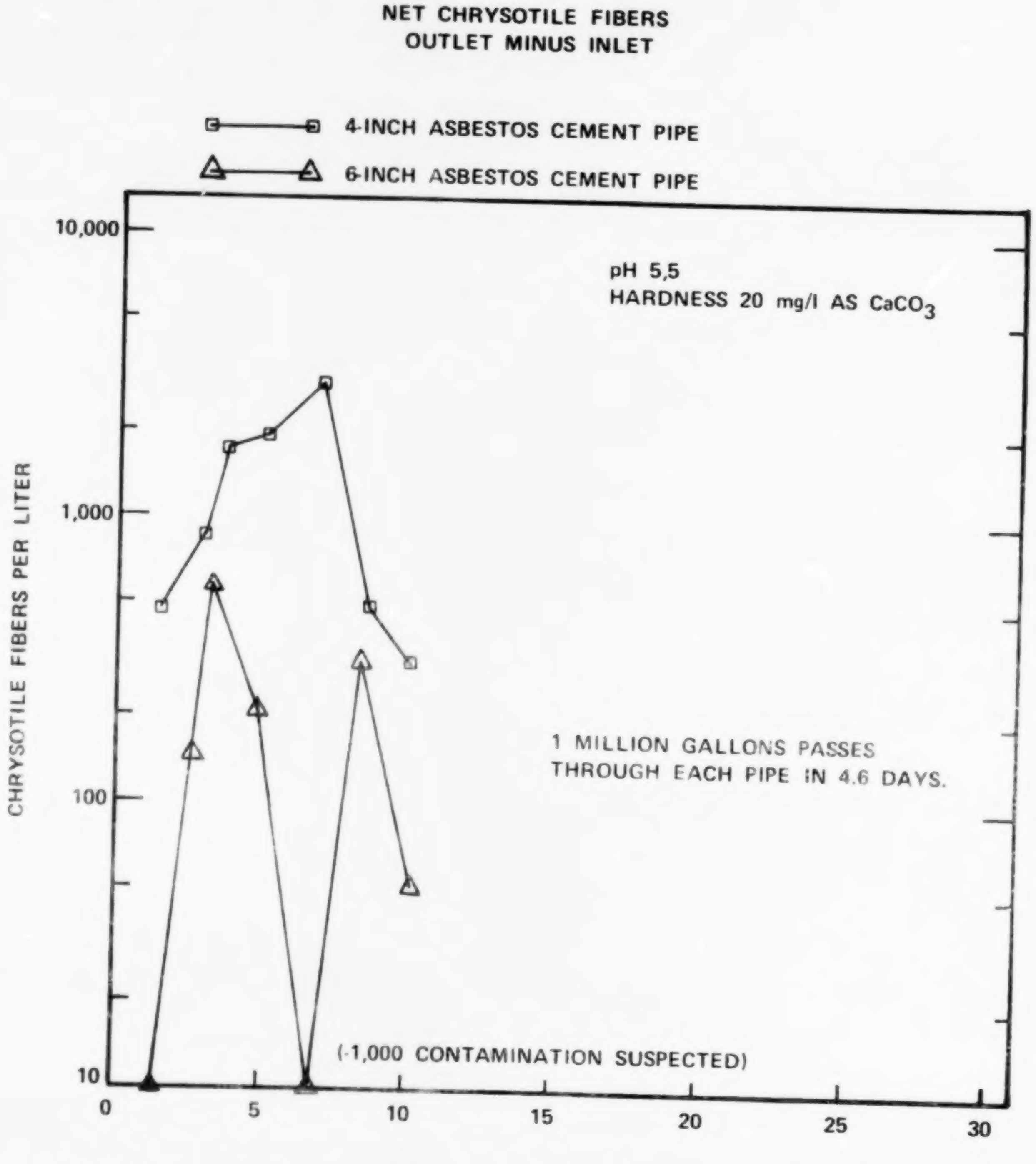

FIGURE 3. CUMULATIVE VOLUME OF WATER THROUGH SYSTEM – GALLONS × 10^6

As can be noted, of 63 supplies analyzed, only nine supplies (14%) had counts over 0.5 x 10^6 fibers per liter and of these, only five (8%) were over 1.0 by 10^6, namely, Duluth, Minn.; North Troy, Vermont; Seattle (Tolt) Washington, Skidaway Isl, Ga., and San Francisco, California. Eleven (18%) had fiber counts below the detection limits of the method.

ACKNOWLEDGEMENTS

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The fifth section on asbestos was prepared by E. McFarren, R. Lishka, J. Millette, G. Logsdon, R. Buelow, J. Agee, J. Symons, P. Cook, G. Glass, B. Fairless.

REFERENCES

1. McCabe, L. J., Symons, J. M., Lee, R. D., and Robeck, G. G. Survey of Community Water Supply Systems, Journal Am. Water Works Assoc. Vol 62(11), 670-687, November 1970.

2. Craun, G. F., and McCabe, L. J., "Overview of Problems Associated with Inorganic Contaminants in Drinking Water." Proceedings National Symposium on the State of America's Drinking Water, Chapel Hill, North Carolina (In Press).

3. Hertsch, F. F. and Maddox, F. D., Fluoridation Practice in Wisconsin, Journal Am. Water Works Assoc., Vol 63, 778-782, 1971.

4. USEPA Report, Chemical Analysis of Interstate Carrier Water Supply Systems, October 1973.

5. Cook, Philip M., Glass, G. E., and Tucker, J. H., "Asbestiform Amphibole Minerals: Detection and Measurement of High Concentrations in Municipal Water Supplies," Science, 185, 853-855 (September 6, 1974).

6. Fairless, B., "Asbestos Fiber Concentrations in the Drinking Water of Communities Using the Western Arm of Lake Superior as a Potable Water Source," U. S. Environmental Protection Agency, Region V, Surveillance and Analysis Laboratory, Chicago, Illinois, 17 pp. Mimeo

7. McFarren, E. F., Millette, J. R. and Lishka, R. J., "Asbestos Analysis by Electron Microscope," In Proceedings AWWA Water Quality Conference, Dallas, Texas, December 1974 (In Press)

APPENDIX VI

PRELIMINARY RESULTS OF PILOT PLANTS TO REMOVE WATER CONTAMINANTS

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APPENDIX VI

PRELIMINARY RESULTS OF PILOT PLANTS TO REMOVE WATER CONTAMINANTS

Table of Contents

Page

A. Introduction 151

B. Treatment for the Removal of Organic Contaminants 151

- 1. Specific Organic Compounds 151
    - a. Literature Reports 151
    - b. Naphthalene 151
    - c. Bis-(2-chloroethyl) ether and Bis-(2-chloroisopropyl) ether 152
    - d. Chloroform, Bromodichloromethane, Dibromochloromethane, and Bromoform 152
    - e. 1,2-Dichloroethane and Carbon Tetrachloride . . 152
    - f. Trihalomethane Precursors 152
        - 1) Description of Pilot Plant 152
        - 2) Chlorination Experiments 155
        - 3) Ozonation Experiments 155
        - 4) Controlled Bench-scale Experiments 158
- 2. General Organics 160
    - a. Pilot Plant 160
    - b. Column Studies 160
        - 1) Upflow-Counter-current 160
        - 2) Upflow-cocurrent 163
- 3. Future Plans 163
    - a. Pilot Plant Studies 163
    - b. Controlled Storage Studies 166
    - c. Column Studies 166
- 4. Acknowledgments 166
- 5. References 166

Page

C. Treatment for the Removal of Trace Metal Contaminants . . 167

1. Introduction 167

2. Research Program 167

a. Jar Tests 167
1) Procedure 167
2) Analytic Methods 168

b. Pilot Plant 168
1) Description and Operation 168
2) Analytic Methods 171

3. Results 171

a. Jar Tests 171
1) Previous work 171
2) Barium 171

b. Pilot Plant Studies 172
1) Mercury 172
2) Cadmium 173
3) Arsenic 173
4) Selenium 174

c. Summary of results 174

4. Radium-226 177

a. Introduction 177
b. Results 177
c. Discussion 177
d. Future Plant 178

5. Acknowledgments 178

6. References 179

D. Treatment for the Removal of Asbestiform Fibers 179

1. Introduction 179

2. Scope of Study 180

Page

3. Experimental Methods and Equipment 180

   a. Equipment 180
   b. Analytical Methods 181

4. Results 182

   a. Raw Water Quality 182
   b. Asbestiform Fiber Removal by Filtration 183

5. Discussion 186

   a. Asbestiform Fiber Removal 186
   b. Efforts to Develop Rapid Detection Methods . . . 195

6. Future Research 195

7. Conclusions 196

8. Acknowledgments 197

9. References 197

PRELIMINARY RESULTS OF PILOT PLANTS TO REMOVE WATER CONTAMINANTS

A. INTRODUCTION

This report will summarize the in-house and out-of-house research conducted by the Standards Attainment Branch of the Water Supply Research Laboratory and their predecessors concerning the treatment technology required for the removal of specific contaminants present in raw water. Because many of these projects are on-going, future plans will also be included. The report will be divided into three general contaminant areas -- organics, inorganics, and asbestos fibers.

B. TREATMENT FOR THE REMOVAL OF ORGANIC CONTAMINANTS

1. Specific Organic Compounds

a. Literature Reports

In 1965, Robeck, Dostal, Cohen and Kreissl[1] demonstrated that coal-base granular activated carbon (GAC) partially exhausted for carbon-chloroform extract (CCE-hf) removal, could reduce the concentration of dieldrin, lindane, 2,4,5-T, DDT, and parathion dosed into river water. In the same year Dostal, Pierson, Hager, and Robeck[2] showed that seven compounds, listed below, present in the Kanawha River water after aeration could be reduced to below detectable concentrations by fresh (2-day old) GAC. These compounds were bis-2(2-chloroethyl) ether, 2-ethylhexanol, bis-(2-chloroisopropyl) ether, α-methylbenzyl alcohol, acetophenone, isophorone and tetralin.

Forty days later, however, all of these compounds with the exception of acetophenone, had broken through the GAC beds to a depth equal to an actual contact time of 3.8 minutes. Providing an additional 1.8 minutes of actual contact time did remove these seven compounds at this time, although another organic, ethyl benzene, was penetrating the GAC to a depth equal to 7.5 minutes of actual contact time -- almost twice that provided in conventionally operated GAC beds.

b. Naphthalene

About 7 months ago, a coal-base GAC column 28 in. deep was constructed, and Cincinnati tap water spiked with approximately 30 µg/l of naphthalene passed down through it at a rate of 2 gpm/ft^2. After 7 months of operation, the NVTOC front has penetrated to the extent that the 50% removal point is approximately 20 in. down the column, whereas the 50% removal point for naphthalene is only approximately 2 in. down the column. This test is continuing.

c. Bis-(2-chloroethyl) ether and Bis-(2-chloroisopropyl) ether

In recent studies, the effluent from a mini-sampler operating on Evansville, Indiana, finished water was analyzed and fresh coal-base GAC was shown to remove all detectable bis-(2-chloroethyl) ether and bis-(2-chloroisopropyl) ether. No information is available on how long GAC would continue to remove this material, however.

d. Chloroform, Bromodichloromethane, Dibromochloromethane and Bromoform

To investigate the ability of GAC to remove chloroform and the other three trihalomethanes two 28-in. deep glass columns were constructed. One contains a coal-base GAC and the other a lignite-base GAC. The columns were arranged such that Cincinnati tap water flowed down through the columns at a rate of about 2 gpm/sq. ft. Figure 1 shows that after 4 weeks of operation the ability of the coal-based GAC to remove chloroform was seriously restricted. The trend of the data from the lignite-base GAC would indicate that its ability to remove chloroform was somewhat greater than the coal-base material.

Figure 2 shows a similar result for bromodichloromethane. The dibromochloromethane concentration applied to these two columns varied between none found and 4 μg/l. None has yet appeared in the effluent from either column. No bromoform was found in the applied water during this study. These two columns were started at different times, however, and therefore received different general organic loads. Whether or not this influenced the trihalomethane removal patterns is not known at this time.

e. 1,2-Dichloroethane and Carbon Tetrachloride

No 1,2-Dichloroethane was found in the Cincinnati tap water during the study. Carbon tetrachloride appeared occasionally at concentrations from <0.2 to 5.6 μg/l in the water applied to the two GAC columns, but none ever appeared in the effluent from either column.

f. Trihalomethane Precursors

1) Description of Pilot Plant

A pilot water treatment plant was constructed of stainless steel, Teflon and glass in order to minimize contamination from structure materials during experimentation on the formation and removal of trihalomethanes. The pilot plant uses untreated Ohio River water as

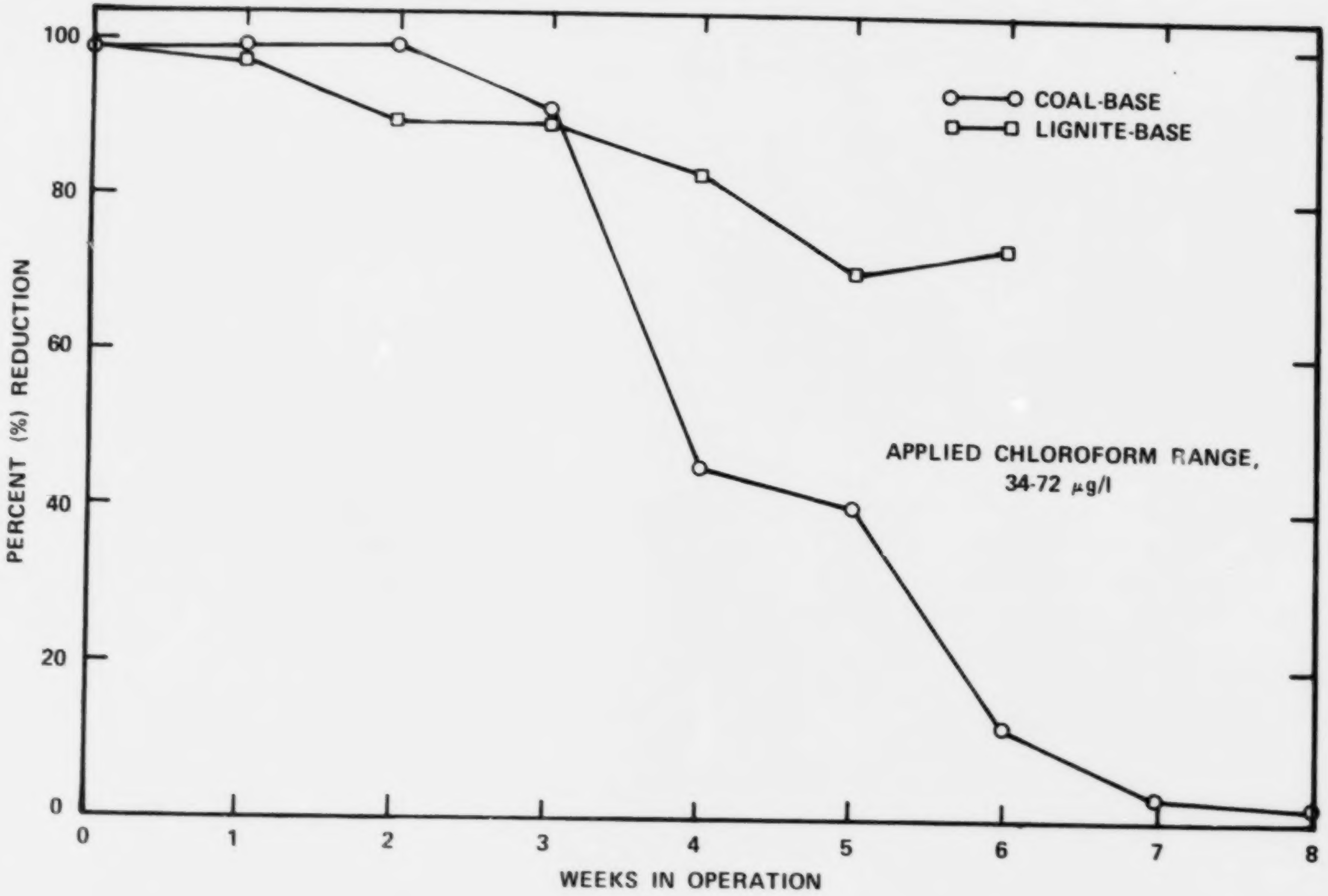

FIGURE 1. REMOVAL OF CHLOROFORM FROM TAP WATER WITH GRANULAR ACTIVATED CARBON

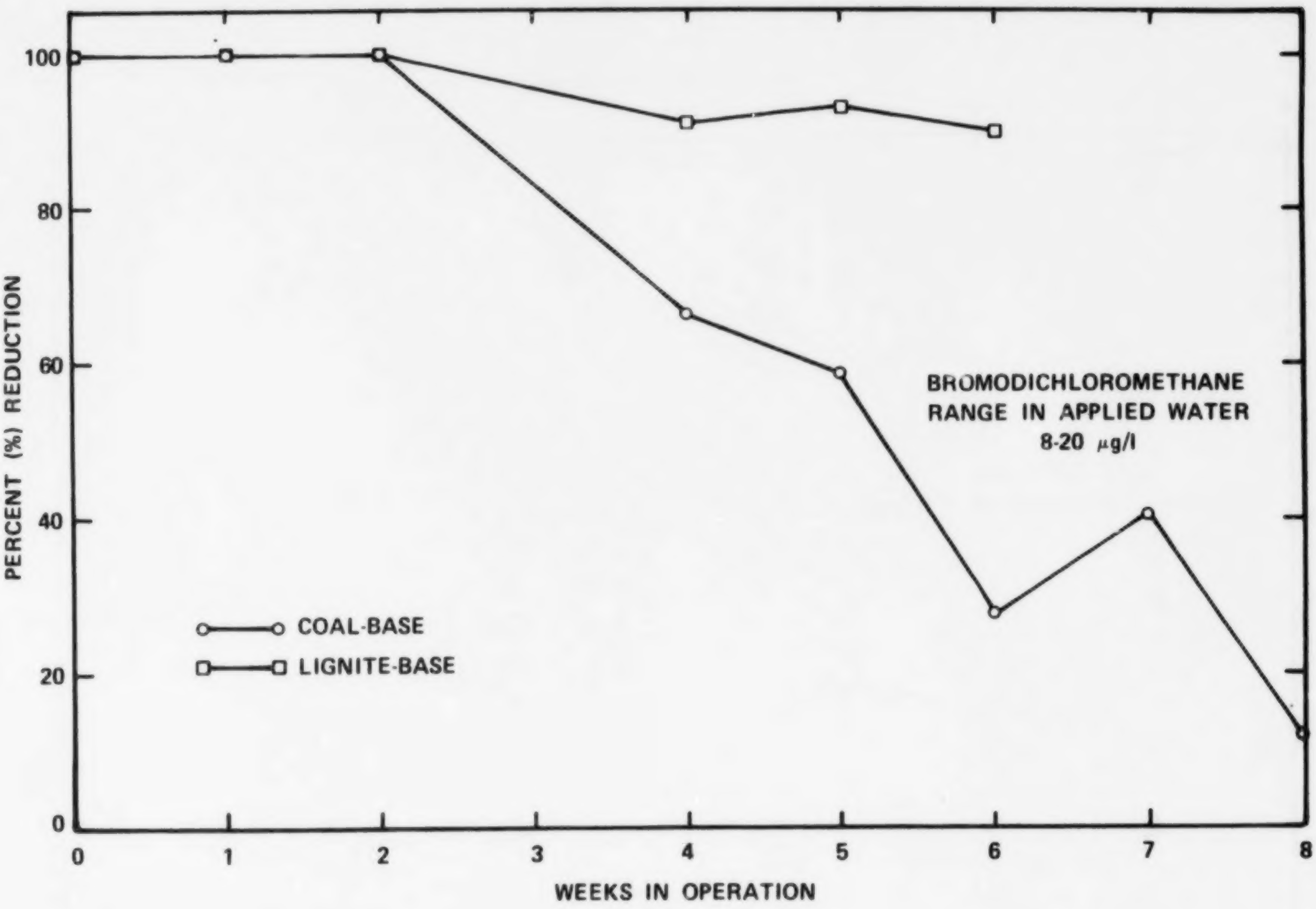

FIGURE 2. REMOVAL OF BROMODICHLOROMETHANE FROM TAP WATER WITH GRANULAR ACTIVATED CARBON

a source, made available through the assistance and cooperation of the Cincinnati Water Works. Following conventional pretreatment with alum (without predisinfection), the settled water flow has been divided between: 1) a dual media (sand/coal) filter (A), 2) a coal-base granular activated carbon filter (B), and 3) a dual-media filter followed by a coal-base granular activated carbon filter (CD). The filtered water is then either ozonated, or chlorinated, or both. Flow, headloss, turbidity, temperature and pH are monitored daily. Figure 3 is a schematic diagram of the pilot plant. Samples for trihalomethane and nonvolatile total organic carbon analysis are collected with zero headspace in muffled, glass vials.

2) Chlorination Experiments

The pilot plant has been running continuously and the first experiments have focused on eliminating the haliform reaction through removal of the precursors with GAC. Using chlorine dosages of 2-3 mg/l and contact times of 30 minutes and 4 days, studies have shown that after 3 to 4 weeks of operation, sufficient materials are being passed through the GAC beds to produce measurable amounts of chloroform (See Table 1). This experiment is continuing.

3) Ozonation Experiments

The purpose of this portion of the organics research project is to determine whether post-ozonation can be used to oxidize trihalomethane precursors to compounds that will not react during post-chlorination. A small (1.5 in diameter) glass contact chamber is used to provide about 5 minutes of contact time between the pilot plant filter effluents and an ozone-oxygen gas mixture. Filter A, B or CD effluents are applied to the top of the contactor, while the ozone-oxygen output from a pilot-plant scale ozone generator is applied at the bottom. Both the gas flowrate and the ozone concentration can be varied. Batches of ozonated effluent are collected for reaction with various chlorine concentrations.

Initially, disinfection-level (0.5-0.7 mg O_3/l H_2O ozone doses, followed by rather high (8 mg Cl_2/l H_2O) post chlorination doses were applied to the filter effluents. When very low (<1 µg/l) chloroform concentrations were produced after a one-half hour chlorine contact period, it was decided to dose and store (at 25°C) effluent samples for a longer time period to follow trihalomethane development. Also, chlorinated effluent samples (without ozonation) would be stored as a control to better show any changes produced by the ozone.

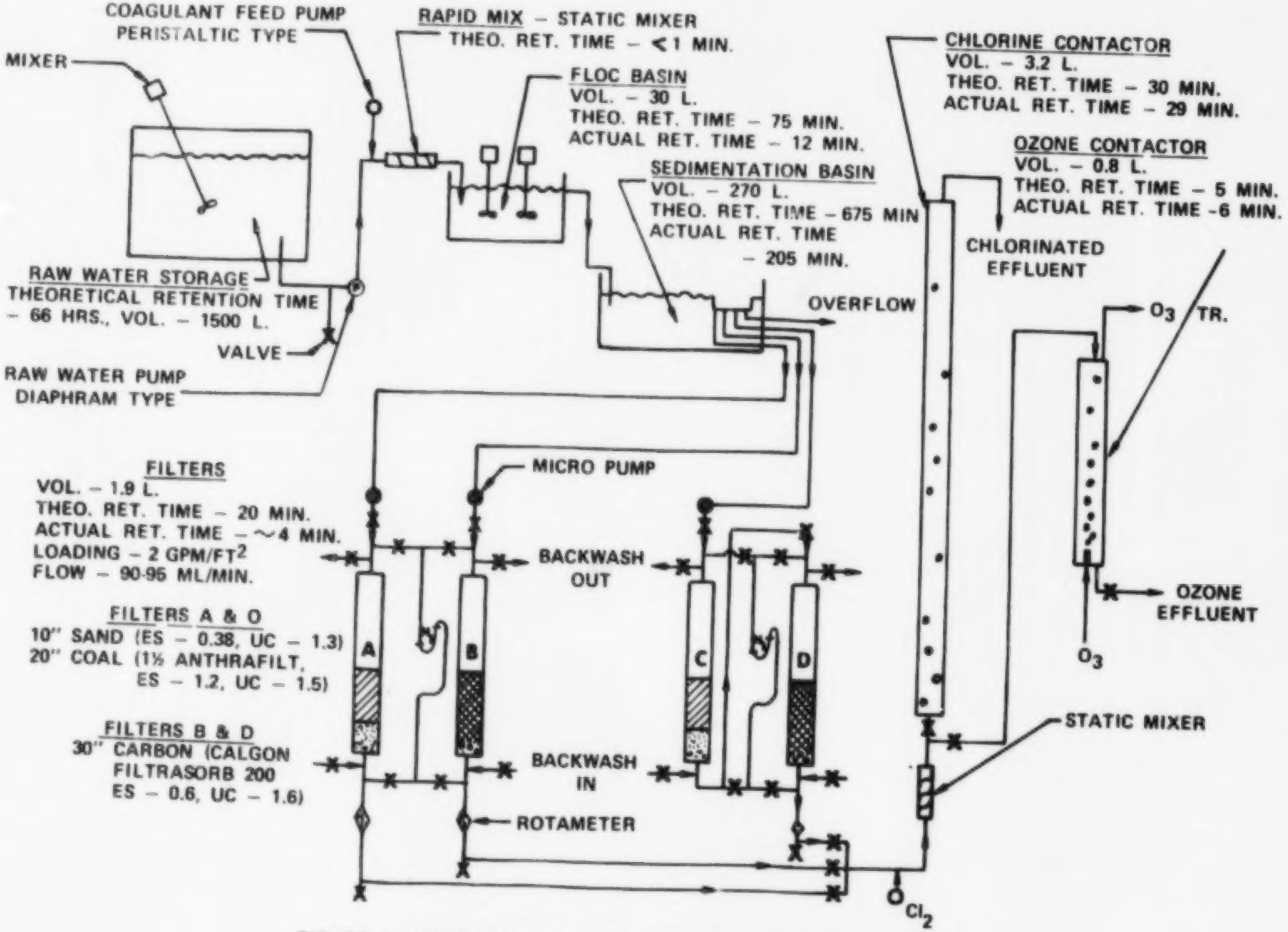

FIGURE 3. STAINLESS STEEL PILOT WATER TREATMENT PLANT

TABLE 1. COMPARISON OF MIXED MEDIA AND GRANULAR ACTIVATED CARBON FOR REMOVING CHLOROFORM PRECURSORS

CHLOROFORM CONCENTRATIONS, μg/l

NON-VOLATILE TOTAL ORGANIC CARBON (NVTOC) CONCENTRATIONS, mg/l

SYSTEM	1ST WEEK Cl_2 CONTACT TIME 30 MIN.	2ND WEEK Cl_2 CONT. TIME 30 MIN. 4 DAY	3RD WEEK Cl_2 CONT. TIME 30 MIN. 4 DAY	4TH WEEK Cl_2 CONT. TIME 30 MIN. 4 DAY	5TH WEEK Cl_2 CONT. TIME 30 MIN. 4 DAY
MIXED MEDIA (SAND/COAL) (A)	2 NVTOC = 1.02	2 13 NVTOC = 0.87	3 13 NVTOC = 0.60	2 16 NVTOC = 1.16	1 10 NVTOC = 0.70
GRANULAR ACTIVATED CARBON (B)	<0.2 NVTOC = <0.05	<0.2 <0.2 NVTOC = <0.05	<0.2 0.5 NVTOC = <0.05	<0.2 2 NVTOC = 0.65	0.2 1 NVTOC = 0.35
MIXED MEDIA FOLLOWED BY GRANULAR ACTIVATED CARBON (CD)	<0.2 NVTOC = <0.05	<0.2 <0.2 NVTOC = <0.05	0.2 0.7 NVTOC = <0.05	<0.2 2 NVTOC = 0.59	<0.2 1 NVTOC = 0.10

The results of this first storage study show that a disinfection-level ozone dose had no apparent effect on the trihalomethane concentrations produced in Filter B and CD effluents after 6 days of storage. In Filter A effluent, ozonation appeared to cause an increase in chloroform concentration and a decrease in bromodichloromethane concentration. See Table 2. This latter situation will receive further study. Other future studies will investigate the effect of higher ozone doses and/or longer ozone contact periods.

4) Controlled Bench-Scale Experiments

In an effort to understand the mechanism of trihalomethane formation and the factors that influence it, experiments are being conducted under controlled conditions in sealed containers changing one variable at a time. At the start of the experiment several containers are prepared in replicate. Periodically over a 7-day period a container is opened and the trihalomethanes measured. Thus the influence of the variable under study on the rate and extent of trihalomethane formation can be determined.

One bench-scale study investigated the formation of trihalomethanes during chlorination of raw and different types of treated water from the Ohio River. This study was conducted in sealed containers at constant pH and 25° Celcius. Some preliminary observations were:

1. When adequate chlorine is added to satisfy chlorine demand for the duration of the experiment, chlorination of raw water yields approximately seven times as much chloroform as does chlorination of the effluent of the dual-media pilot plant filter (A) and approximately 80 times as much as does chlorination of the effluent of the fresh GAC filter (B) (207μg/l, 32 μg/l, and 2.7 μg/l, respectively, in 7+ days). The reason the chloroform production is so low in filter effluent compared to the raw water is not known at this time, but in future studies settled water will be included in the series to determine at what step in treatment the precursors are removed.

2. Of the trihalomethanes under study, chloroform is formed in the highest concentration with bromodichloromethane and dibromochloromethane following in approximate rations of 100:15:1.

3. With the waters tested, those with a higher chlorine demand gave a greater trihalomethane concentration upon chlorination, but trihalomethane formation accounted for only about 3% of the chlorine consumed. Therefore other chlorination by-products are being formed, both organic and inorganic.

TABLE 2

SUMMARY OF OZONATION EXPERIMENT

Sample	Chlorine Contact Time	Chloroform	Bromodichloromethane	Dibromochloromethane	Bromoform
A + Cl_2	1/2 hour	4	NF	NF	NF
A + Cl_2	6 days	6	14	4	NF
A + O_3 + Cl_2	1/2 hour	NF	NF	NF	NF
A + O_3 + Cl_2	6 days	15	8	3	NF
B + Cl_2	1/2 hour	0.3	NF	NF	NF
B + Cl_2	6 days	2	3	<1	NF
B + O_3 + Cl_2	1/2 hour	NF	NF	NF	NF
B + O_3 + Cl_2	6 days	3	3	2	NF
CD + Cl_2	1/2 hour	0.2	NF	NF	NF
CD + Cl_2	6 days	2	3	<1	NF
CD + O_3 + Cl_2	1/2 hour	0.2	NF	NF	NF
CD + O_3 + Cl_2	6 days	2	4	<1	NF

NF = None Found

All Trihalomethane Concentrations in μg/l

4. In all waters tested, trihalomethane production continued as long as a measurable chlorine residual was present, but at a decreasing rate. The initial rate of chloroform formation in the raw river water was about 10 μg/l/hr for the first six hours. The rate of formation was very low, however, for GAC effluent throughout the 7+ days.

2. General Organics

The monitoring of specific organics may be beyond the capability of most water utilities for some time to come. Therefore, treatment for the removal of specific organics may be accomplished by providing treatment that will produce a water with a very low concentration of a general organic parameter such as non-volatile total organic carbon, although monitoring for specific organics is the only method of assuring their removal.

a. Pilot Plant

In addition to the study of the elimination of trihalomethane precursors, NVTOC concentrations are being measured at various stages of the pilot plant in an attempt to determine under what conditions very low NVTOC concentration water can be produced for extended periods of time.

Figure 4 shows the average relative concentrations of non-volatile total organic carbon at various stages of treatment for the first three weeks of operation and operational weeks three to six. Figure 5 compares the percent removal of NVTOC by coal-base GAC, both with and without prefiltration of the influent water. The presence of carryover floc in the influent to filter B is not interfering with NVTOC removal.

b. Column Studies

1) Upflow-counter-current

The objective of this study is to determine if low concentrations of NVTOC can be continuously maintained in the effluent of a GAC filter by periodic removal of a portion of the exhausted GAC, replacing it with fresh GAC. A small (1.5 in diameter) glass column has been placed in operation. Cincinnati tap water (approximately 80 ml/min) is applied to the bottom of the column, flows upward through the GAC bed, and overflows from the top of the column to a volume measuring device. When the effluent NVTOC limit is exceeded, one-half of the GAC bed is removed (as a slurry) from the bottom of the column. and an equal quantity of fresh GAC is added at the top.

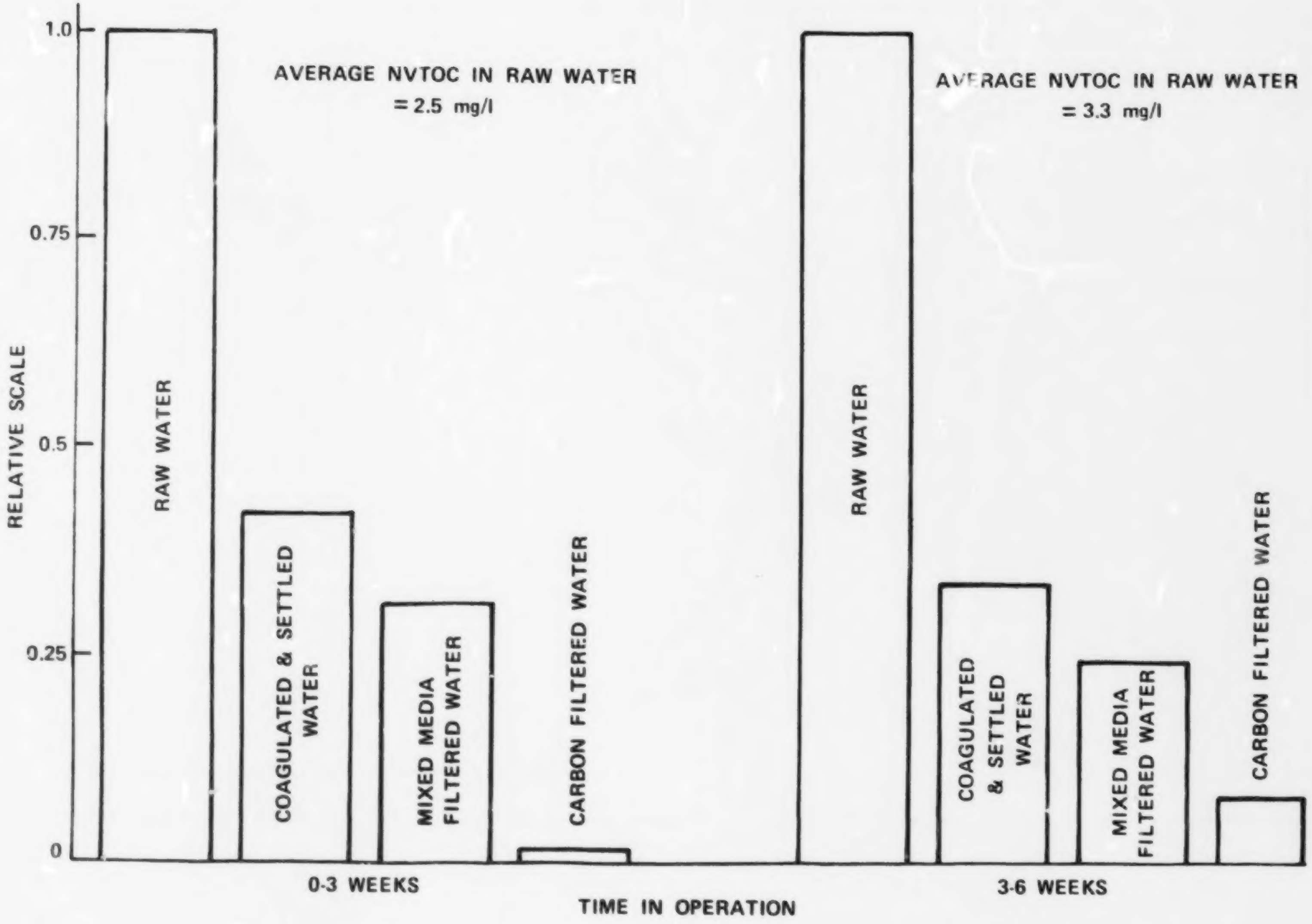

FIGURE 4. RELATIVE NON-VOLATILE TOTAL ORGANIC CARBON REMOVAL DURING WATER TREATMENT

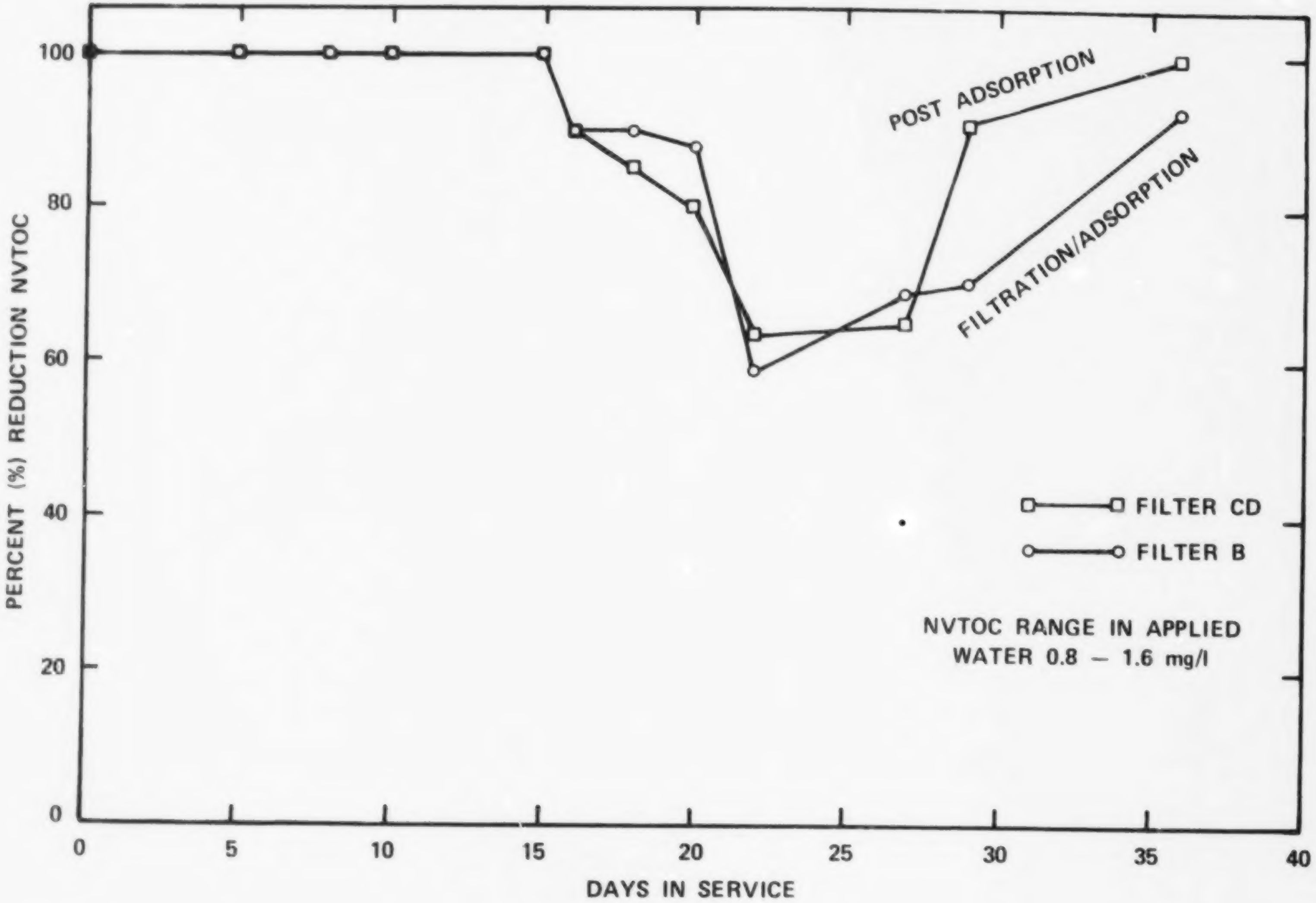

FIGURE 5. FILTRATION/ADSORPTION VS. POST ADSORPTION FOR NON-VOLATILE TOTAL ORGANIC CARBON REMOVAL

For the initial test series, an 8-inch bed of GAC was chosen. Preliminary observations, after 20 days of operation, include:

1. The effluent NVTOC limit can be maintained for only 2-3 days before GAC removal and addition is necessary.

2. Exhaustion of the GAC bed appears to occur much more rapidly than in similar downflow beds, indicating possible wall effects and/or flow channelization within the column.

This study will continue, with future efforts directed toward deeper GAC beds and/or larger diameter columns. Thus far a 16-inch deep bed is performing more reliably.

2) Upflow - Co-current

In an attempt to compare the performance of various types of GAC, six 3-inch diameter, 18-inch long columns were filled with six different types of GAC produced by three different manufacturers. Cincinnati tap water was continuously passed upflow through each column at a rate of about 3 gpm/sq ft for 32 weeks. The influent and effluent concentrations of NVTOC and carbon-chloroform extract (CCE-m) were monitored weekly during this time. Data from each column were averaged for several four-week intervals and plotted in Figures 6 and 7. All of the data fell within the envelopes shown, indicating that the type of GAC had little influence on performance. These data also show that the life of the GAC in these columns was fairly short for the removal of these two parameters. References 3 and 4 contain additional information on the performance of activated carbon.

3. Future Plans

a. Pilot Plant Studies

Current chlorination and ozonation studies will continue to determine how the aging of the GAC columns will alter the trihalomethane formation patterns. When these experiments are completed they will be repeated using lignite-base GAC in the columns. Possible future studies will cover the influence of powdered activated carbon, pre-disinfection with chlorine or ozone, addition of chlorine just prior to filtration, and the use of chlorine dioxide. Also studies on removal of raw water contaminants will be conducted.

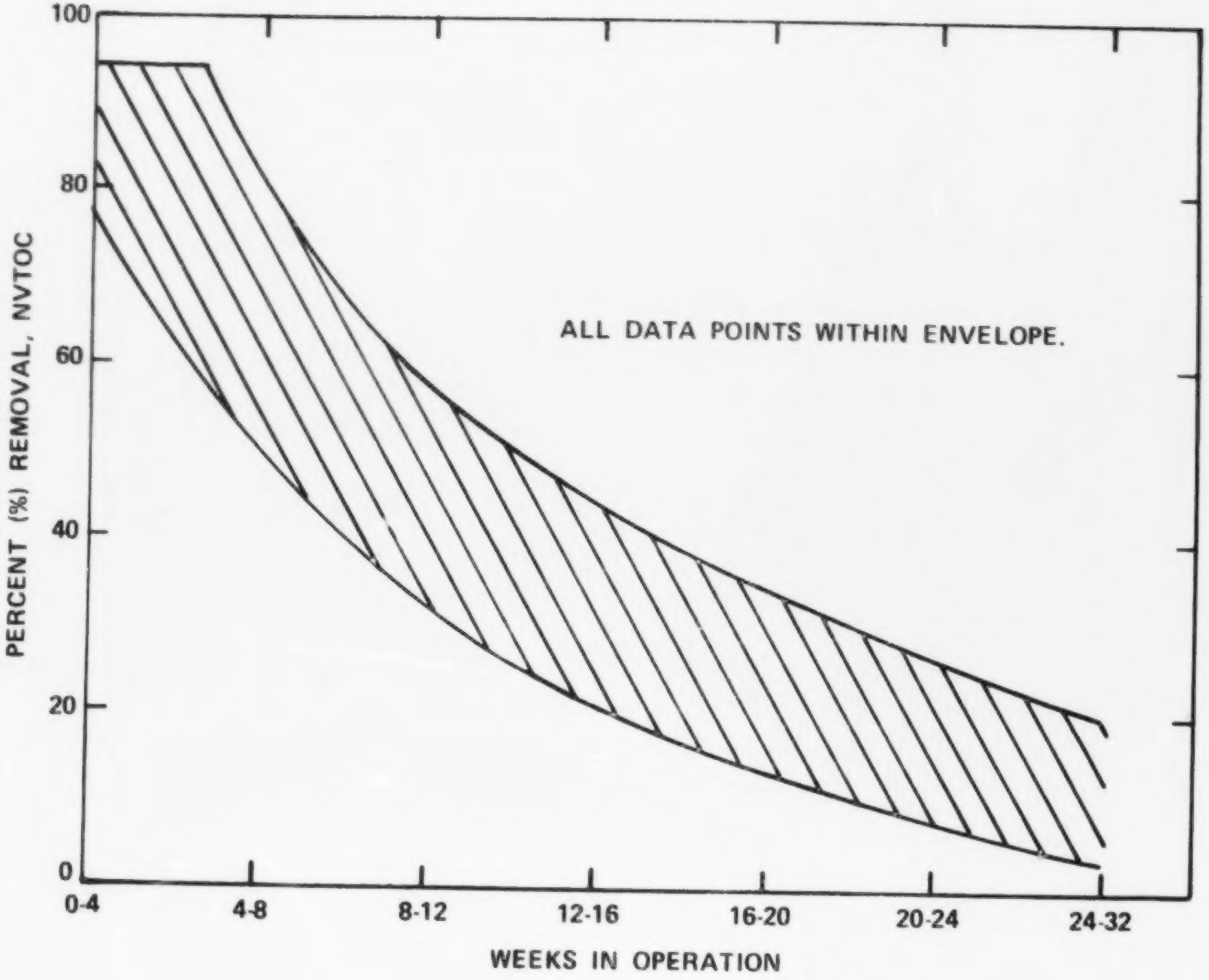

FIGURE 6. NON-VOLATILE TOTAL ORGANIC CARBON REMOVAL FOR SIX TYPES OF GRANULAR ACTIVATED CARBON

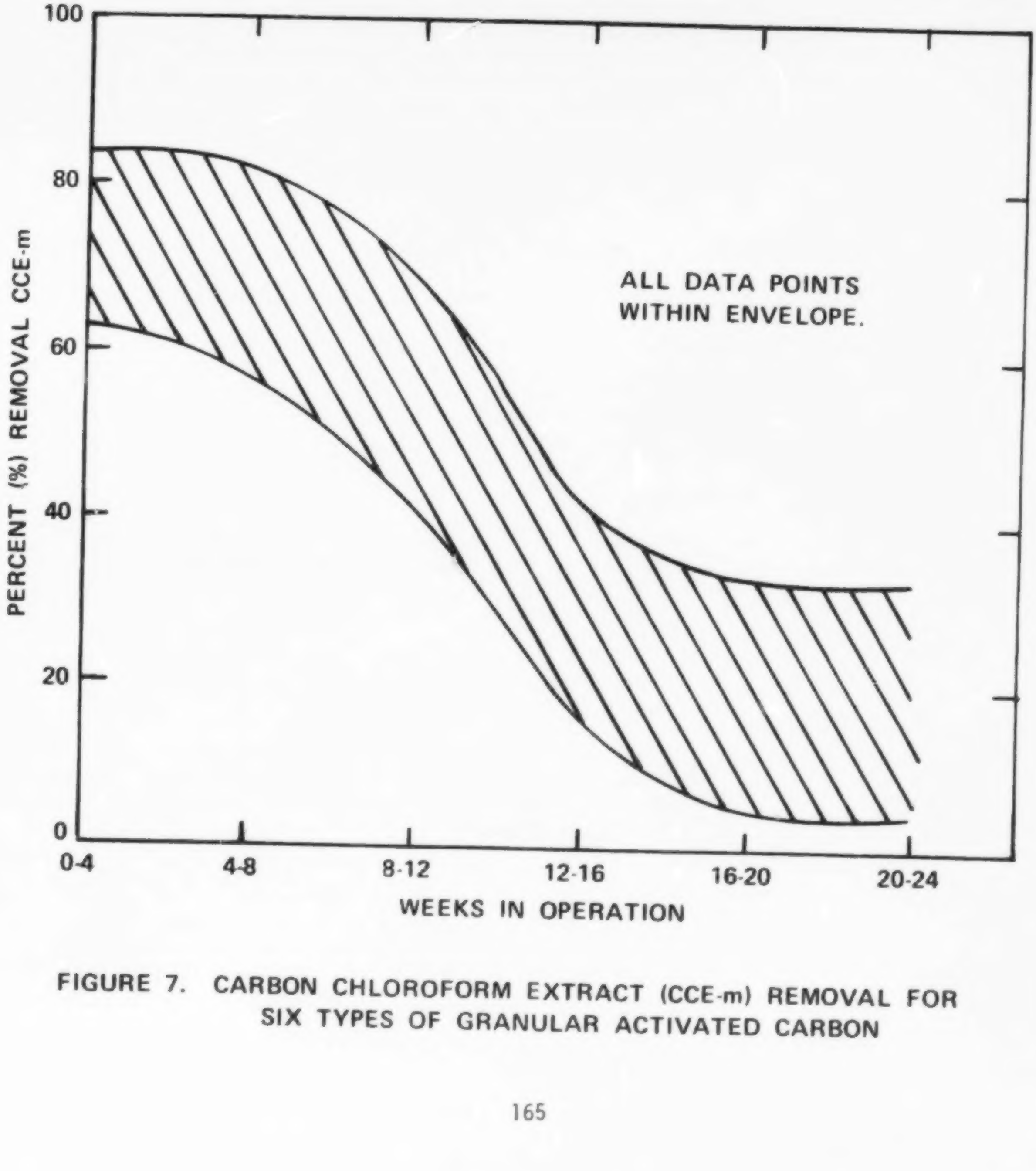

FIGURE 7. CARBON CHLOROFORM EXTRACT (CCE-m) REMOVAL FOR SIX TYPES OF GRANULAR ACTIVATED CARBON

b. Controlled Storage Studies

Possible future controlled storage studies will include experiments on chlorination of specific trihalomethane precursors and the influence of temperature and form and concentration of chlorine residual on the formation of trihalomethane. Also other chlorination by-products will be studied to follow-up on the finding that nitromethane becomes chloropicrin and m-xylene becomes chlorxylene upon chlorination.

c. Column Studies

Work will continue studying the ability of columns of GAC operated upflow, downflow, co-, and counter-current to effectively remove organics as measured by general organic parameters.

Because the column test described in the Naphthalene Section B(1)(b) was so successful, it will be repeated using other compounds. Possible candidates are: benzene, bis-(2-chlorethyl) ether, carbon tetrachloride, phthalic anhydride, beta-chloroethylmethyl ether, octadecane, DDT, dieldrin and aldrin.

5. References

1. Robeck, G.G., Dostal, K.A., Cohen, J. and Kreissl, J.F., "Effectiveness of Water Treatment Processes in Pesticide Removal," Journal American Water Works Association, 57, 2, 181-199 (February 1965).

2. Dostal, K.A., Pierson, R.C., Hager, D.G. and Robeck, G.G., "Carbon Bed Design Criteria Study at Nitor, West Virginia," JAWWA, 57, 5, 663-674 (May 1965).

3. Activated Carbon in Water Treatment, University of Reading Conference, April 3-5, 1973. The Water Research Association, Medmenham, Marlow, Buckinghamshire, SL7, 2HD, United Kingdom.

4. Love, O.T., Jr., Carswell, J.K., Stevens, A.A., and Symons, J.M., "Evaluation of Activated Carbon as a Drinking Water Treatment Unit Process," Water Supply Research Laboratory, United States Environmental Protection Agency, Cincinnati, Ohio, March 1975, 17 pp Mimeo.

C. TREATMENT FOR THE REMOVAL OF TRACE METAL CONTAMINANTS

1. Introduction

The Federal Proposed Interim Drinking Water Regulations (IDWR)[1] established limits for a number of substances in water including various trace metals. For many years, these limits were rarely exceeded and, therefore, knowledge on treatment methods to remove these contaminants from water was of only minor concern. In recent years, however, the awareness of trace metal contamination has increased for various reasons, including improved analytical procedures and more frequent and comprehensive surveillance activities. As a result, this awareness has stimulated the interest and concern for information and knowledge on the removal of trace metals from water by conventional treatment methods.

In anticipation and response to the need for this information, the Water Supply Research Laboratory, U. S. Environmental Protection Agency developed a research program on the removal of trace inorganic substances in water by conventional treatment processes. The trace metals in the IDWR that have been, or are presently being studied are mercury, barium, arsenic, selenium, cadmium and radium*. Chromium and lead will be studied in the near future.

2. Research Program

The WSRL research program consists of two phases: (1) experiments in the laboratory using jar test apparatus and (2) pilot plant tests using a 2 gpm water treatment pilot plant.

a. Jar Tests

1) Procedure

The laboratory jar test methods have been described in detail by Logsdon and Symons[2]. The waters used in the jar test work were raw Ohio River water; raw well water from Glendale, Ohio; Cincinnati tap water; and a Midwestern groundwater containing barium. Except for the barium-laden water, the test waters were dosed with the contaminant to be studied, given 2 minutes of rapid mix after addition of the treatment chemical and 20 minutes of slow mix for the coagulation test, or they were given 3 minutes of rapid mix and 30 minutes of slow mix for softening. One hour of settling was used for all tests. Analyses were made for pH, turbidity, alkalinity, and in some cases, hardness, as well as for contaminant concentration.

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*Note: The radium research will be treated separately.

2) Analytic Methods

Two methods were used for metal analyses. An atomic absorption spectrophotometer was used for analysis of non-radioactive contaminants in portions of the mercury, barium, and arsenic work, and occasionally in the selenium experiments. These methods have been described by Kopp et al.[3], McFarren[4], and Caldwell, et al.[5] In some experiments, radiotracers were used with stable carriers. Radioactivity was measured using a shielded NaI (Tl) crystal and single-channel analyzer. When radiotracers were used, the initial contaminant concentration was determined by adding the radioisotope, plus a known volume of stock carrier solution, to the water being treated and calculating the initial metal concentration. The removal percentage was taken as equal to the percentage of reduction of radioactivity.

b. Pilot Plant

1) Description and Operation

The WSRL pilot plant is capable of treating in parallel two 2 gpm flows of water. The plant has been designed to operate in a number of different configurations, but has been run primarily in a conventional manner for the metal removal studies with rapid mixing, flocculation, sedimentation, and rapid granular filtration.

The test waters used so far, Cincinnati tap water and raw well water from Glendale, Ohio, were stored in a 7500-gallon stainless steel tank. This water was pumped to a constant-head tank that had an overflow line back to the storage tank. Water to be treated was pumped at 2.1 gpm through two rapid mix tanks having a theoretical detention time of about 2 minutes each. In the first mixing tank, the contaminants and, if required, soda ash for pH control, were added. The coagulant, Ferrifloc, alum, or lime for softening experiments, was introduced into the second mixing tank.

After the rapid mix, the water was flocculated for one hour in a mechanically mixed flocculation basin, and then settled for about 6.5 hours (theoretical detention times). Except for excess lime softening experiments, the settled water was then filtered through either one or two parallel filter columns (4 1/4-inch diameter) at a rate of 4 gpm/sq ft. The filters were: (1) a dual-media filter containing 20 inches of No. 1 1/4 Anthrafilt over 12 in. of 0.4mm effective size Muscatine sand and (2) a granular activated carbon filter containing 30 inches of lignite-base, 0.8-0.9 mm effective size, granular activated carbon. When excess lime softening tests were run, the settled water was recarbonated to pH about 9.6 and settled (6.5 hours theoretical detention time) in a second sedimentation basin before being filtered. Figures 1 and 2 are schematic diagrams of the pilot plant.

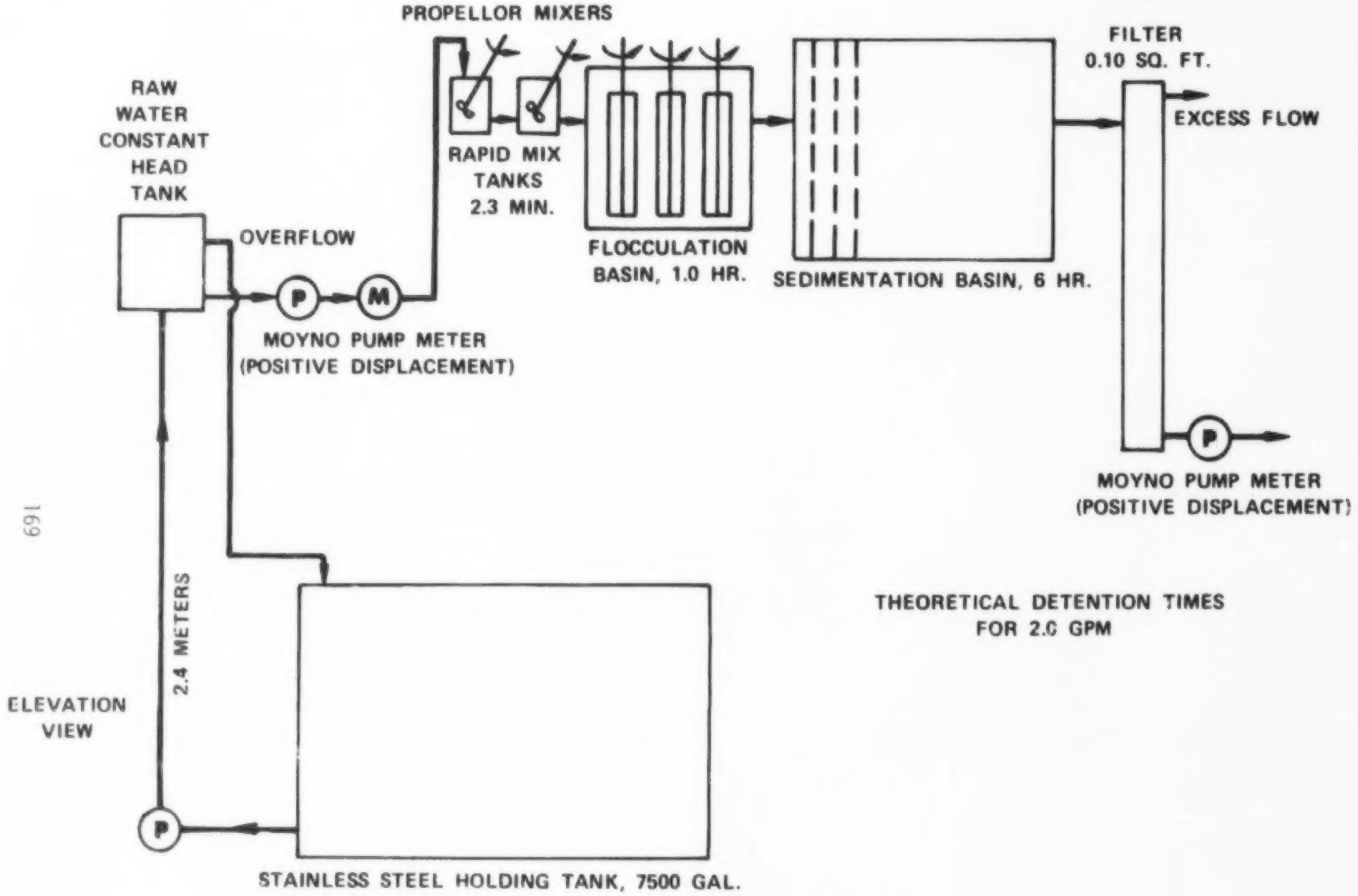
PROPELLOR MIXERS
RAW WATER CONSTANT HEAD TANK
OVERFLOW
P
M
MOYNO PUMP METER (POSITIVE DISPLACEMENT)
RAPID MIX TANKS 2.3 MIN.
FLOCCULATION BASIN, 1.0 HR.
SEDIMENTATION BASIN, 6 HR.
FILTER 0.10 SQ. FT.
EXCESS FLOW
P
MOYNO PUMP METER (POSITIVE DISPLACEMENT)
THEORETICAL DETENTION TIMES FOR 2.0 GPM
2.4 METERS
ELEVATION VIEW
P
STAINLESS STEEL HOLDING TANK, 7500 GAL.

FIGURE 1

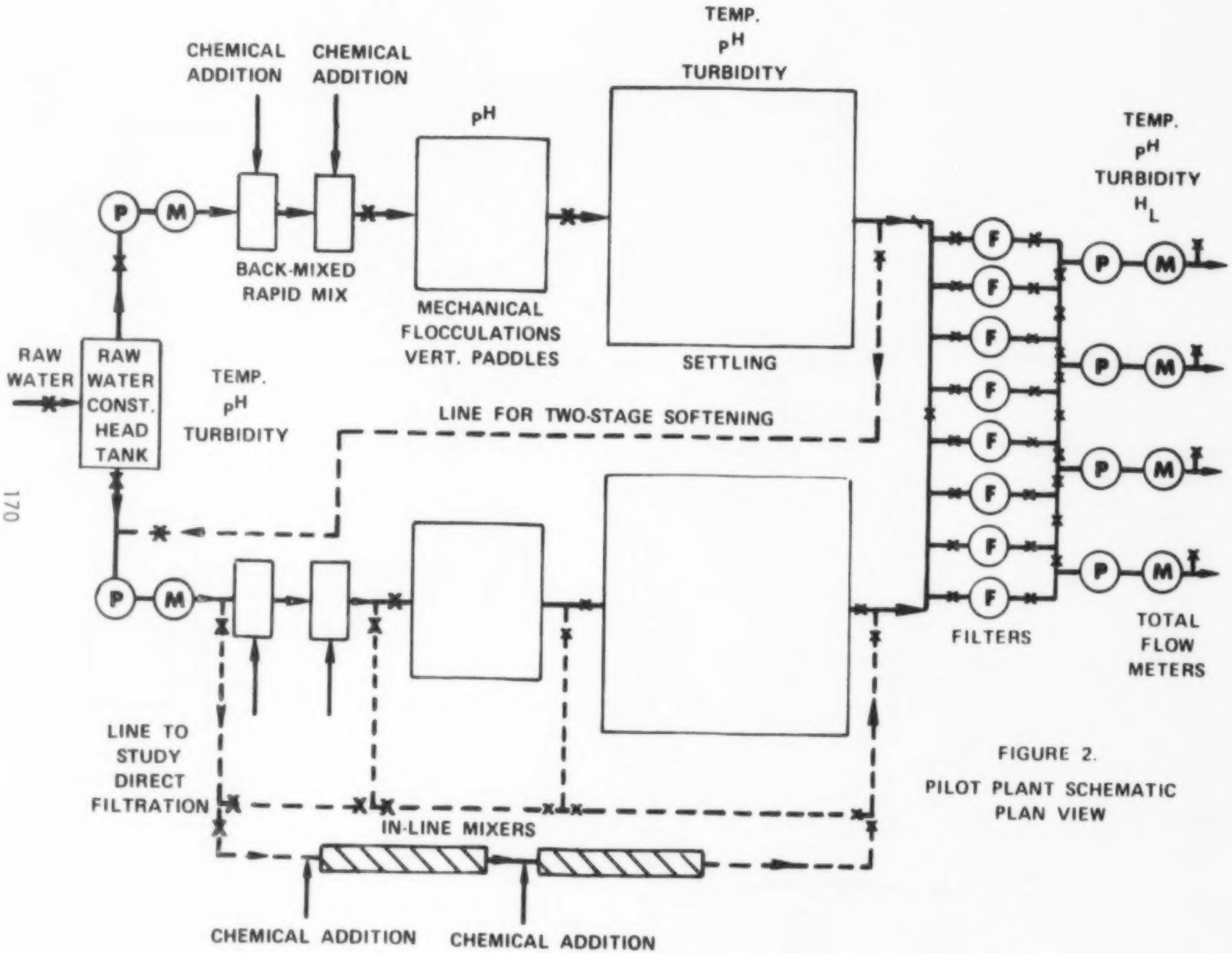

FIGURE 2.

PILOT PLANT SCHEMATIC
PLAN VIEW

Initially, the plant ran continuously for 40 hours (∿ 5000 gallons treated water), but later the time was lengthened to about 100 hours (∿ 12,000 gallons treated water). Grab samples of raw, settled, and filtered water were obtained periodically in 1-liter cubitainers and preserved with 1.5 ml of concentrated nitric acid prior to analysis.

2) Analytic Methods

Mercury analysis was done by the flameless atomic absorption method.[3] Arsenic and cadmium analysis was done on a Perkin Elmer Model 403 Atomic Absorption Spectrophotometer equipped with a graphite furnace and a Perkin Elmer Model HGA-2000 controller. Selenium analysis was done using the method of Caldwell et al.[5]

3. Results

a. Jar Tests

1) Previous Work

Jar test studies have been completed on mercury, barium, arsenic, selenium and cadmium. Pilot plant tests, on the other hand, have been only partially completed for mercury, arsenic, selenium, and cadmium. Because the results of most of the jar test experiments have been presented in detail by Logsdon and Symons[2,6] and by Logsdon, Sorg and Symons[7], they will not be repeated.

2) Barium

The jar test work on barium removal has been completed, but the pilot plant studies have not begun. The laboratory experiments used a midwestern ground water containing 7 to 8 mg/l of barium. Coagulation with aluminum sulfate and ferric sulfate was expected to remove barium effectively because the producton of rather insoluble barium sulfate was anticipated. However, the anticipated results were not achieved; removals did not exceed 30 percent with either type of coagulant. A possible explanation for the poor removal was supersaturation of barium sulfate. A series of two-stage coagulation experiments were carried out using 100 mg/l of coagulant initially and a 20 mg/l dose for the second stage. These studies produced higher barium removals, giving support to the suggestion that barium sulfate was supersaturated after the first stage of coagulation. Unfortunately, such treatment would not be very practical because of the higher cost required of two-stage treatment.

Barium removal by lime softening was also studied. In the pH range of 10-11, barium removals exceeded 90 percent; the maximum removal was near 98 percent. Data from a full-scale ion-exchange softening plant also showed a 98 percent barium reduction when the initial barium content was about 11 mg/l.

Finally, laboratory tests showed that 400 mg/liter of Activex resin could remove about 80 percent of the barium, but that powdered activated carbon was not effective for barium removal.

b. Pilot Plant Studies

The test waters used in the pilot plant studies to date were Cincinnati tap water and well water from Glendale, Ohio. The treatment methods used were alum coagulation, Ferrifloc coagulation, and lime softening.

1) Mercury

Two types of mercury were selected for study: mercuric chloride (inorganic form) and methyl mercury chloride (organic form). Pilot plant test results on inorganics using spiked Cincinnati tap water generally agreed with the jar test data. For raw water concentrations of 4.0-7.5 μg/l, removals for settled water ranged from 24 to 70 percent and for filtered water (dual-media) 47 to 80 percent when the water was coagulated with 15-72 mg/l of Ferrifloc. When alum (22 to 62 mg/l) was used as a coagulant, removals were less than 10 percent for both settled and filtered water.

Organic mercury removal by activated carbon in combination with Ferrifloc was studied using Cincinnati tap water spiked with 3.7 to 5.6 μg/l of mercury. The treatment consisted of adding 4.5 to 5.6 mg/l of powdered carbon in the first rapid mix tank and 28-35 mg/l of Ferrifloc in the second rapid mix tank. The mercury removal results ranged from 5 to 32 percent for settled water; 8 to 38 percent for dual media filtered water and; 98 to 100 percent for granular activated carbon filtered water.

Lime softening pilot plant tests using raw well water have been only partially completed. Preliminary test data, however, have shown removals for both types of mercury to be significantly higher than those achieved in the jar test experiments. Inorganic mercury removals were 10-40 percent higher than in the jar tests with the settled water, ranging from 45 to 63 percent and filtered water (dual media) from 69 to 90 percent. When organic mercury was studied, early test results indicated that some mercury was being removed, as compared to no removal in the jar tests. Additional lime softening work will be carried out to determine the reason for the differences.

2) Cadmium

Pilot plant studies have been completed on cadmium using Cincinnati tap water and the raw well water. In all cases, the results were in agreement with the jar test data.

The tests showed that cadmium removal was pH dependent for both alum and Ferrifloc coagulation using Cincinnati tap water spiked with 0.028 - 0.032 mg/l of cadmium. For example, when Ferrifloc was used as the coagulant, removals for the settled water was 20-26 percent at pH 6.8 and 70-80 percent at pH 8.3. Removals for dual media filtration was about 5-10 percent higher than the settled water.

Lime softening at pH 9.5 and 11.3 was also studied. Cadmium removals at both pH values were over 95 percent for the settled water, dual media filtered water, and granular carbon filtered water.

An eight-week series of direct filtration tests were also carried out using two granular activated carbon filters and Cincinnati tap water spiked with 0.028-0.032 mg/l of cadmium.

Each test run lasted about 100 hours and the filters were not backwashed between runs. Cadmium removals ranged from 7 to 30 percent for the filter containing 30 inches of Filtrasorb 100 and 17 to 54 percent for the filter containing 30 inches of exhausted Filtrasorb 200.

3) Arsenic

Two forms of arsenic have been studied, Arsenic III (arsenite) and Arsenic V (arsenate). Because As(III) would probably be found in ground water, the behavior of As(III) was studied using only the raw well water. Pilot plant tests on As(V) however, were carried out using both Cincinnati tap water and the raw well water. In all cases, the arsenic concentration was near 0.40 mg/l and results compared very closely with the jar test data.

Arsenic III removal by lime softening was investigated at pH 9.5 and 11.3. At pH 9.5, removal for the settled water was 10 percent and for the filtered water 24 percent (GAC) and 26 percent (dual-media). When the water was softened to 11.3, settled water removal was 63 percent and filtered water removal 72 percent for both filters. Although pilot plant tests have not been run to confirm it, laboratory jar tests showed that when As(III) is oxidized to As(V) using chlorine, As(III) behaves like As(V). Because higher removals were obtained on As(V) under all treatment processes studied, arsenite should, therefore, be oxidized to arsenate before removal is attempted.

Removal of As(V) was studied in the pilot plant using alum, Ferrifloc and lime. Arsenic removals using Cincinnati tap water and Ferrifloc were excellent; settled water removals were 91-94 percent and filtered water (dual media) removals were greater than 98 percent. When alum was used as the coagulant, removals were somewhat less; settled water removals ranged from 75 to 86 percent and filtered water (dual media) removals ranged from 85 to 96 percent.

Softening tests on the raw well water were also investigated at pH 9.5 and 11.3. At pH 9.5, the test data showed an As(V) removal of 49 percent for the settled water and 53 percent for the filtered waters. At pH 11.3, As(V) removals were above 98 percent for both settled and filtered waters.

4) Selenium

The behavior of two forms of selenium has been studied, selenium IV (selenite) and selenium VI (selenate). Although the jar test studies have been completed, only limited pilot plant work has been carried out. Because selenite has been identified as a problem in some ground waters, SE(IV) was investigated primarily with raw well water. Removals of 0.1 mg/l of SE(IV) by lime softening in the laboratory did not exceed 40 to 50 percent and generally were lower. Coagulation studies with alum and Ferrifloc were also undertaken with well water and a surface water. The results of these laboratory experiments found that Ferrifloc produced higher removals than alum and that removals for both coagulants decreases as the pH increases from 6 to 8. Removals ranged from about 80 to 20 percent with Ferrifloc and were 10 percent or less with alum when 25 mg/l of coagulant was used.

The removal of selenate (VI) was uniformly poor for all jar test and pilot plant studies. Selenate removal by coagulation with iron or alum (up to 100 mg/l of coagulant), by softening from pH 9 to 10.8 or by treatment with up to 100 mg/l of powdered activated carbon was less than 10 percent for initial selenium concentrations of 0.1 mg/l. Although conventional treatment experiments were unsuccessful in removing selenate, a short reverse osmosis test showed that this technique could remove it and merits further investigations. During a two-hour reverse osmosis test run on Cincinnati tap water spiked with 0.1 mg/l of selenium VI, over 97 percent of the selenium was removed by the R.O. unit operating at 1.5 liters/minute.

a. Summary of Results

Table I summarizes all of the jar test and pilot plant data collected thus far. These studies are continuing.

TABLE I

SUMMARY OF RESULTS OF TREATMENT PROCESSES TO REMOVE TRACE METALS FROM DRINKING WATER

	Coagulation		Softening		Absorption
Trace Metal	Alum	Ferric Sulfate	Lime pH 9.5-10	Excess lime pH 10.6-11	Activated Carbon
		Jar Test Data			
Mercury (0)* CH_3HgCl	Poor**	Poor	Poor	Poor	Good†
Mercury (I), $HgCl_2$	Poor	Fair	Fair	Good†	Good
Barium	Poor	Poor	Good	Good to very good†	Poor
			Zeolite field data - very good†		
Selenium(I) Se^{+4}	Poor pH<7	Fair to good pH<7	Poor	Fair	Poor
Selenium(I) Se^{+6}	Poor	Poor	Poor	Poor	Poor
Arsenic(I), As^{+3}	Poor	Fair to good†	Poor	Good†	Poor
Arsenic(I), As^{+5}	Good to† very good pH<8	Good to† very good pH<8	Good	Very good†	Poor
Cadmium(I)	Poor to Fair	Good to† very good pH>7.5	Very good†	Very good†	-
		Pilot Plant Data			
Mercury (0) CH_3HgCl	-	-	-	-	-

Table 1 (continued)

Trace Metal	Coagulation		Softening		Absorption
	Alum	Ferric Sulfate	Lime pH 9.5-10	Excess lime pH 10.6-11	Activated Carbon
Mercury(I) $HgCl_2$	Poor	Fair	-	Good	-
Barium	-	-	-	-	-
Selenium(I) Se^{+4}	-	-	Poor to Fair	-	-
Selenium(I), Se^{+6}	-	Poor	-	-	-
Arsenic(I), As^{+3}	-	-	Poor	Good	-
Arsenic(I), As^{+5}	Good to† very good	Very† good	Fair	Very Good†	Poor to Fair
Cadmium(I)	Poor to fair	Good pH 8.4	Very good†	Very good†	-

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* - (O) = Organic; (I) = Inorganic

** - Key - Poor=0-30% removal; Fair=30-60% removal; Good=60-90% removal; Very good = above 90% removal.

† - Best treatment techniques.

- Not yet tested.

4. Radium-226

a. Introduction

Radium-226 is found in some waters of the USA in excess of the 1962 Public Health Service Drinking Water Standards limit of 3 pCi/l. If the new Federal Drinking Water Regulations set an even lower limit for Ra-226, additional water sources would need treatment to meet the standard.

Radium-226 is usually found in groundwaters, because it is a geochemical contaminant. It is associated with certain aquifers such as St. Peter sandstone in the upper Mississippi Valley and Cheyenne sandstone in Colorado and New Mexico[8]. Radium-226 may be found in surface waters contaminated by radium-bearing springs. Other sources of contamination are leachates from tailings of uranium milling plants[9] and from the phosphate rock mining and milling industry in Florida.

Because Ra-226 more frequently is found in ground waters, treatment processes used for ground water are of interest. Some basic information on removal of radium was contained in Straub's report.[8]

b. Results

A recent study of water treatment plants in Iowa has shown results similar to those reported by Straub.[8] The Radiochemistry and Nuclear Engineering Facility (R&NEF), a part of the EPA's Office of Radiation Programs has contracts with the states of Iowa and Illinois for studying radium removal by water plants. The following results have been obtained in the Iowa study to date and are presented in Table II.

c. Discussion

On the basis of Iowa data, Ra-226 removals of about 75% could be anticipated for lime softening. If greater removal is needed, ion exchange or reverse osmosis treatment would be necessary. In either case, the practice of blending raw and treated water to obtain a less corrosive water and save capital costs by reducing plant size could result in a plant effluent having an excessive concentration of Ra-226. In such a case, corrosion control would have to be accomplished by methods other than raw water blending, and softening 100% of plant flow would increase costs at existing softening plants that now bypass some raw water.

RADIUM REMOVAL BY WATER TREATMENT PROCESSES

Treatment Technique	Radium raw	pCi/l finished	% reduction
Greensand for iron removal	6.9	6.7	7%
Iron removal - aeration and pressure filtration	16	12	25%
Lime-soda softening	6.1	0.9	85%
	9.3	2.3	75%
Iron removal followed by ion exchange softening	49	1.9	96%
	5.7	0.3	95%
	6.7	0.2	97%
	12	0.5	96%
Reverse osmosis	14	0.6	96%

d. Future Plans

Radium removal research contracts are continuing under the management of R&NEF with water supply engineering input from WSRL. In addition, WSRL has under consideration a grant application for development of detailed construction and operating cost data and estimates for water treatment plants built and operated primarily for radium removal.

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6. References

1. Interim Primary Drinking Water Standards, Federal Register, Volume 40, No. 51, Part II, p. 11190-11198, March 14, 1975.

2. Logsdon, G.S. and J. M. Symons, *Journal American Water Works Association*, *65*, 554 (1973).

3. Kopp, J.F., M. C. Longbottom and L. B. Lobring. *JAWWA*, *64*, 20 (1972).

4. McFarren, E. F., *JAWWA*, *64*, 28 (1972).

5. Caldwell, J.S., R.J. Lishka and E. F. McFarren, *JAWWA*, *65*, 731 (1973).

6. Logsdon, G.S. and J.M. Symons, Removal of Trace Inorganics by Drinking Water Treatment Unit Processes. Water-1973. American Institute of Chemical Engineers Symposium Series, *70*, 136 367-377, (1974).

7. Logsdon, G.S., T.J. Sorg, and J.M. Symons, *Removal of Heavy Metals by Conventional Treatment, Proceedings 16th Water Quality Conference - Trace Metals in Water Supplies: Occurrance, Significance and Control*, University of Illinois Bulletin, *71*, 108, 111-133 (April 29, 1974).

8. Straub, C.P., Radium-226 and Water Supplies: Cost-Benefit-Risk Appraisal, Unpublished Report, 1973.

9. Tsivoglou, E.C. and O'Connell, R.L., Waste Guide for the Uranium Milling Industry, DHEW, USPHS, DWSPC, RATSEC, Technical Report, W62-12.

D. TREATMENT FOR REMOVAL OF ASBESTIFORM FIBERS

1. Introduction

The presence of asbestiform fibers in the drinking water of communities using western Lake Superior as a water source was made known in the summer of 1973. In the fall and early winter of that year an interagency agreement for studies of the problem was formulated and signed by the U. S. Environmental Protection Agency and the U. S. Army Corps of Engineers. Under this agreement EPA funded the pilot plant research on

6. References

1. Interim Primary Drinking Water Standards, Federal Register, Volume 40, No. 51, Part II, p. 11190-11198, March 14, 1975.

2. Logsdon, G.S. and J. M. Symons, Journal American Water Works Association, 65, 554 (1973).

3. Kopp, J.F., M. C. Longbottom and L. B. Lobring. JAWWA, 64, 20 (1972).

4. McFarren, E. F., JAWWA, 64, 28 (1972).

5. Caldwell, J.S., R.J. Lishka and E. F. McFarren, JAWWA, 65, 731 (1973).

6. Logsdon, G.S. and J.M. Symons, Removal of Trace Inorganics by Drinking Water Treatment Unit Processes. Water-1973. American Institute of Chemical Engineers Symposium Series, 70, 136 367-377, (1974).

7. Logsdon, G.S., T.J. Sorg, and J.M. Symons, Removal of Heavy Metals by Conventional Treatment, Proceedings 16th Water Quality Conference - Trace Metals in Water Supplies: Occurrance, Significance and Control, University of Illinois Bulletin, 71, 108, 111-133 (April 29, 1974).

8. Straub, C.P., Radium-226 and Water Supplies: Cost-Benefit-Risk Appraisal, Unpublished Report, 1973.

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The pilot plant research was conducted at the Lakewood Pumping Station in Duluth, with the assistance of the Department of Water and Gas of the City of Duluth. Pilot plant operations were conducted in the period from April through September 1974. In this time a total of 227 granular media and 228 diatomaceous earth (DE) filter runs were conducted.

2. Scope of Study

There were two principal objectives in the research. First, the pilot plants were to be operated in such a way that data needed for engineering design and cost estimates could be obtained. The results and conclusions related to design and cost factors are being presented by Robinson et al.[1] A paper on DE filtration optimization is being presented by Baumann.[2] The second objective of the study was to obtain information on the removal of asbestiform fibers. That information is presented in this paper.

In order to learn how to reduce the asbestiform fiber count by filtration, a number of variables were studied. Those common to both granular and DE filtration were filtration rate, seasonal conditions, and raw water turbidity. Other important variables in the granular filtration study were filtration with and without sedimentation, dual media vs. mixed (tri) media, doses and combinations of inorganic salts and organic polymers, single-stage vs. multi-stage flash mixing, and flash mix chambers vs. in-line mixers. Variables important in the DE study were one-step vs. two-step precoating, vacuum vs. pressure filtration, DE conditioning with alum or polymers, and body feed doses.

3. Experimental Methods and Equipment

a. Equipment

The apparatus used in the research has been described in the

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*Duluth-Superior Urban Study, Interim Report on Water Supply for the Duluth-Superior-Cloquet Area, A Joint Study by the U. S. Army Corps of Engineers, St. Paul District, and the U. S. Environmental Protection Agency (March, 1975).

EPA report on the project.[3] Two types of filters, granular media and DE, were used. All units were situated in Lakewood Pump Station. Raw water for all units was drawn from the wet well at the pump station. Total water flow through individual filter systems generally ranged from 10 to 20 gpm.

Two granular filters were employed. Both units were Water Boy package plants with 4.0 square feet of filter surface. Equipment variations with these units included use of dual media, mixed media, no settling, tube settlers, single-stage rapid mix and two-stage rapid mix with propellor mixers, two-stage and three-stage rapid mix with in-line mixers, alum or ferric chloride as the primary coagulant, anionic, cationic, and non-ionic polymers, and filtration rates from 2 to 7 gpm/sf.

Two kinds of DE filter systems were employed. Pressure filtration was carried out with an Erdlator filter. In this unit water was not coagulated and settled, contrary to U. S. Army practice, but the clear Lake Superior water merely passed through the pretreatment portions of the Erdlator on its way to the pressure filter. The Erdlator had two pressure vessels, each containing six cylindrical septa. Total filter surface area for one pressure vessel was 10.0 square feet. After the filter septum was precoated, body feed could be added dry or in slurry form.

The gravity, or vacuum DE filter unit consisted of an open rectangular tank with flat septa. The driving force for filtration was the difference between atmospheric pressure and the pressure at the pump intake on the effluent side of the filter. Filter surface was also 10.0 square feet on this unit. Body feed could be added dry or in slurry form.

Both kinds of DE filters were operated in various ways in order to evaluate conditioning of DE with alum, cationic polymer and anionic polymer. On some runs a cationic polymer was added to the raw water. Single-step vs. two-step precoat was studied. Conditioned DE was used in precoat situations as well as for body feed. Various grades of DE, from fine to coarse, were evaluated.

b. Analytical Methods.

Most of the analytical procedures were done in accordance with Standard Methods[4]. In addition to laboratory turbidity measurements on grab samples, continuous flow turbidity data were obtained with both 90° scatter and 15° forward scatter instruments. Grab samples were obtained for the analyses, including asbestos. Since there is no standard method for asbestiform fibers in water, analytical methods were different for each laboratory used. Three analytical laboratories were involved in this study.

The National Water Quality Laboratory of EPA in Duluth analyzed raw and filtered samples for suspended solids and amphibole mass. The x-ray diffraction technique for amphibole mass has been published by Cook. Although this method measured only amphibole mass irrespective of shape (by definition fibers have a length:width ratio of 3:1 or greater), and did not measure chrysotile, the availability of amphibole mass data within a few days of sample collection made this method a valuable tool.

Transmission electron microscope analysis of water samples was done at the Ontario Research Foundation (ORF) and at the University of Minnesota at Duluth (UMD). The ORF analytical method has been published[6]. ORF obtained size information on each fiber (length and width) and confirmed that all fibers were amphibole or chrysotile by electron diffraction. Electron diffraction was used to identify a portion, but not all, of the fibers counted by UMD.[7]

4. Results

The results of all pilot plant filter runs and analyses are presented in the EPA filtration report and appendices. The data presented in this paper relate principally to the problems of asbestiform fiber removal by filtration. Relevant raw water data are also presented in order to place the filtration results in proper perspective.

a. Raw Water Quality

Water quality parameters of greatest interest in this study were turbidity, asbestiform fiber count, and amphibole mass. Other data on pH, alkalinity, hardness, temperature, and suspended solids can be found in the EPA report.

Most turbidity measurements were made with a Hach 2100A laboratory turbidimeter. When a comparison was made between a Monitek in-line turbidimeter and the Hach 2100A, it was found that although the numerical readings differed for the two instruments (15° forward scatter vs. 90° scatter), the trends of turbidity variation were quite similar. Both instruments showed rising or declining turbidities at the same time. These data were presented in the EPA report.

Turbidity of the raw water at Lakewood changed very little during most of the five months of pilot plant operation. Except for a period extending from 2300 hours on June 6 to 0700 hours on June 15, 1974, and other briefer periods, the turbidity of the raw water from the Lakewood Intake ranged from 0.35 to 1.0 TU. During the period beginning on June 6, the raw water turbidity ranged from 1.6 to 6.3 TU and averaged 2.7 TU. Other periods of raw water turbidity in excess of 1.0 TU were relatively short, ranging from a period of 2 hours to one of 29 hours, with the raw water turbidity seldom exceeding 1.5 TU during these periods.

The turbidity of the raw water transported from the Cloquet Pipeline Intake was not as low as that from the Lakewood Intake, but it also varied only over a slight range. The turbidity of the Cloquet raw water tested was never below 2.0 TU nor above 4.0 TU.

Asbestiform fiber count and amphibole mass concentrations showed much greater variation than raw water turbidity. Fiber counts and amphibole mass concentrations are plotted vs. time in Figures 1 and 2 to show the time variation of these parameters.

It should be mentioned that there were no violent storms during the pilot plant operation, and in the fall and winter of 1974, amphibole mass concentrations exceeding 1.0 mg/l were measured during a storm. The pilot plant was shut down two or three months before the worst water conditions (high turbidity and fiber count) occurred because funds for conducting the study were limited.

During the May-September period of operation, amphibole and chrysotile fiber counts were frequently in the 0.5 to 1.5 x 10^6 f/l range, and amphibole mass often ranged between 0.05 and 0.2 mg/l. There were extremes both above and below these values.

b. Asbestiform Fiber Removal by Filtration

It is apparent from the portions of this paper that deal with the scope of the study and the equipment used that there were numerous variations in experimental conditions. In order to simplify data analysis, amphibole mass and asbestiform fiber removal results are presented for treatment categories that specify such variables as: filter media, filtration rate, use of sedimentation, inorganic coagulant and polymer, and type of rapid mixing for granular filtration; and number of layers of precoat, precoat conditioning, body feed conditioning, and polymer feed to raw water for DE filtration. Tables 1, 2 and 3 show summarized results for dual media, mixed media, and diatomite filtration.

The treatment data are given in terms of the number of filtered samples submitted for analysis and the number of samples with a

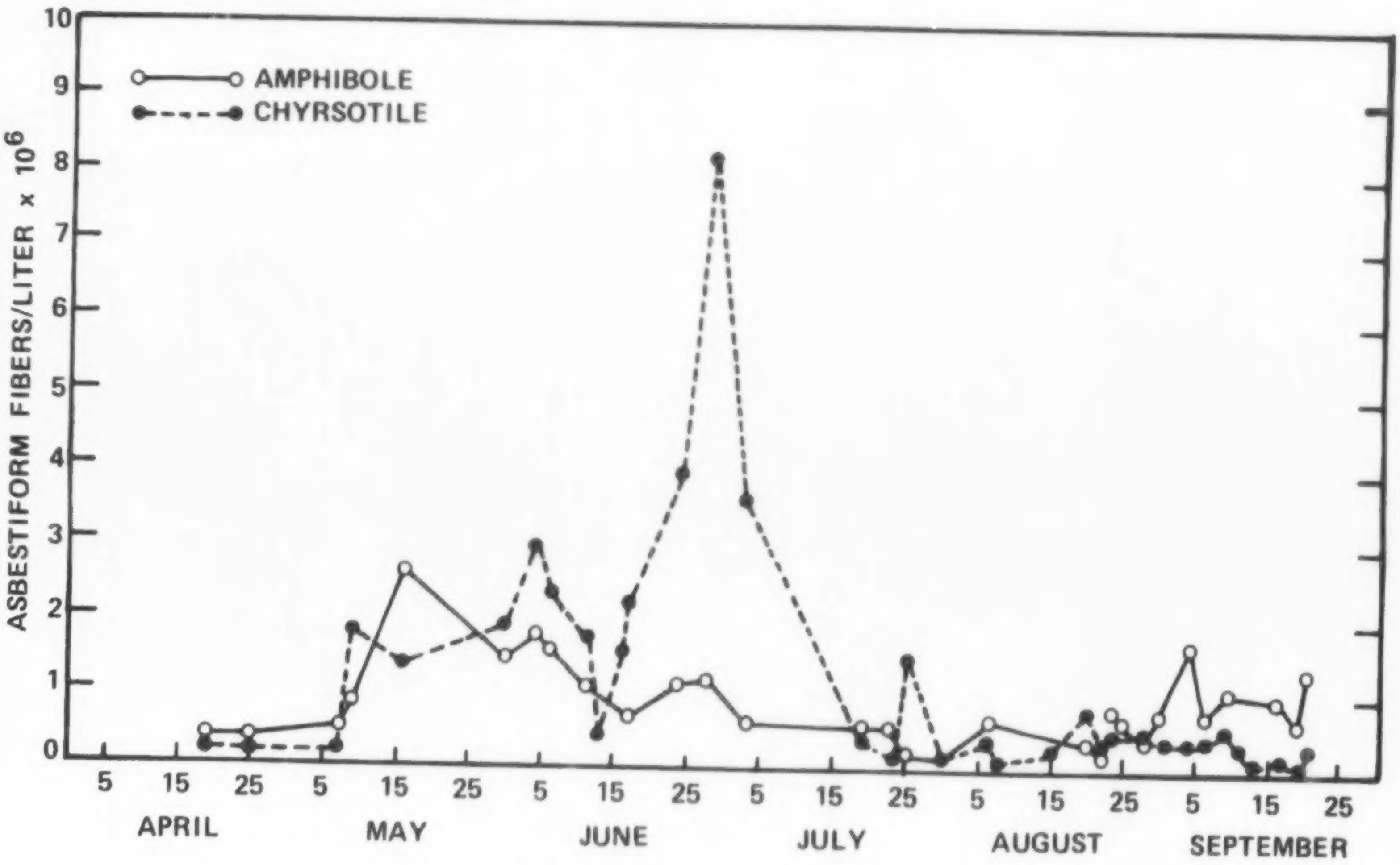

FIGURE 1. ONTARIO RESEARCH FOUNDATION
ASBESTIFORM FIBER COUNTS
RAW WATER AT DULUTH LAKEWOOD INTAKE - 1974

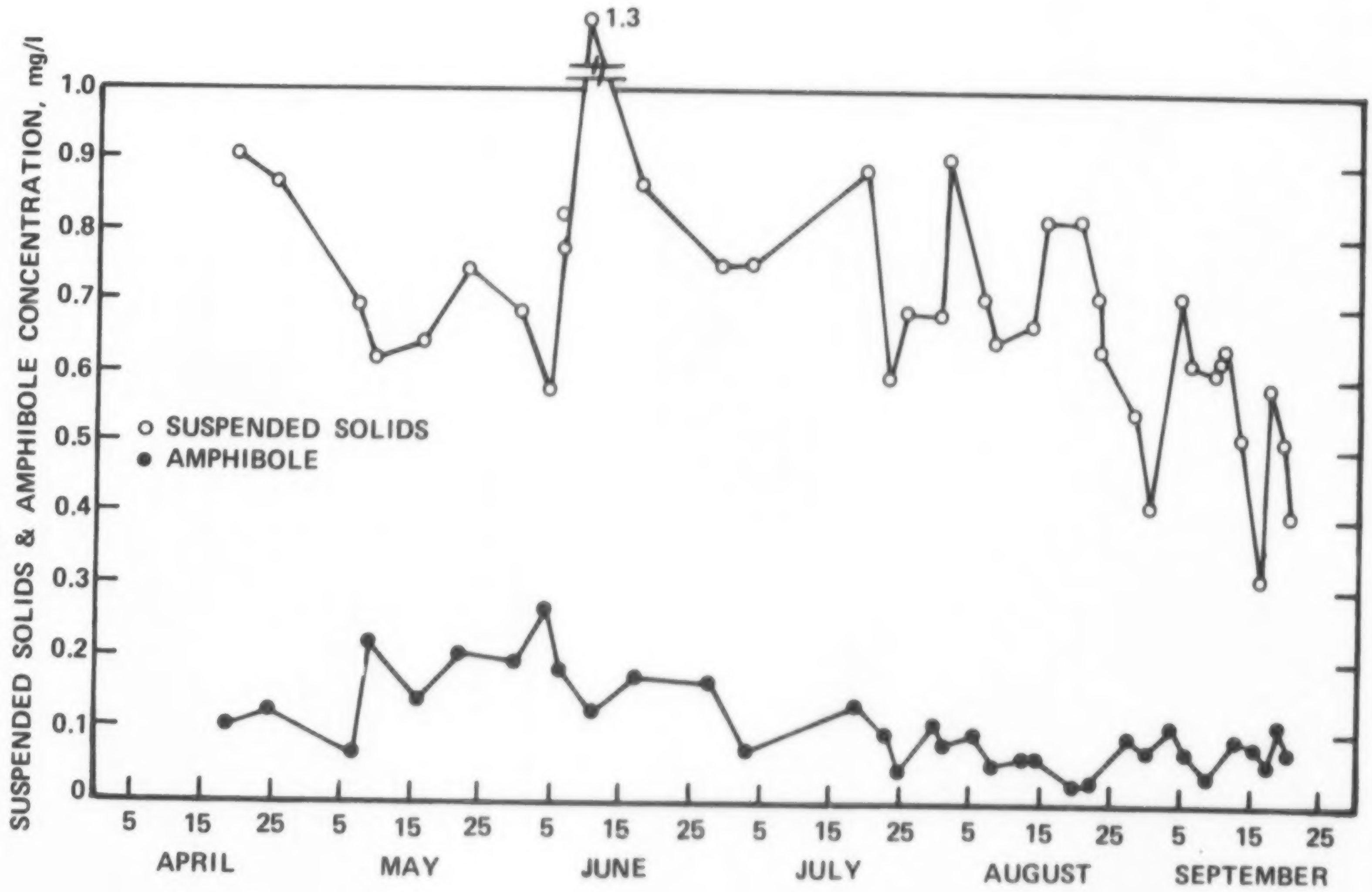

FIGURE 2. ENVIRONMENTAL PROTECTION AGENCY
NATIONAL WATER QUALITY LABORATORY
AMPHIBOLE MASS CONCENTRATION
RAW WATER AT DULUTH LAKEWOOD INTAKE - 1974

result equal to or less than 0.04 x 10^6 fibers/liter (f/l) (fiber data from ORF), or equal to or less than 0.005 mg/l in the case of amphibole mass data. The amphibole mass detection limit varied according to the volume of the water sample filtered for analysis. Waters which had a greater tendency to clog membrane filters had higher detection limits. If the detection limit was above 0.005 mg/l, it became impossible to say whether the amphibole mass in a treated water exceeded 0.005 mg/l. Samples clouded in this uncertainty were not tabulated in the results presented herein. For example, in Table 1, treatment category filtration without sedimentation, alum and nonionic polymer, ~4 gpm/sf, ten samples are listed as having been analyzed for asbestiform fibers, while only five are listed as having been analyzed for amphibole mass. The other five amphibole mass samples had a detection limit that exceeded 0.005 mg/l.

Tables 1, 2 and 3 show that the more successful variations of filtration, whether dual media, mixed media, or diatomite, produced effluents having amphibole mass concentrations and amphibole fiber counts near the detection limits of the analytical methods employed. Chrysotile fiber count in filtered water generally exceeded 0.04 x 10^6 f/l for dual media filtration tests and for DE filtration tests not employing polymer conditioning. Mixed media filter runs employing alum and nonionic polymer or alum, anionic polymer and another polymer, and diatomite runs employing A-23 conditioning of DE or Catfloc B conditioning of raw water did have some runs with effluent chrysotile counts $\leq 0.04 \times 10^6$.

5. Discussion

a. Asbestiform Fiber Removal

The initial objective of the filtration research at Lakewood Pumping Station was the removal of amphibole asbestiform fibers and turbidity-causing suspended matter. According to the pilot plant research contract, the principal criterion for successful treatment will be the economical attainment of virtually complete removal of asbestos-like fibers as defined by optical and electron microscope analysis using the best current state of the art. A secondary criterion shall be the production of water having a turbidity of not more than one turbidity unit.[8] The fibers referred to in the contract were expected to be principally amphibole.

In conversations between the WSRL and EPA Region V (Chicago)[9], which was then heavily involved with contracts for analysis of asbestiform fiber content of water samples, the Ontario Research Foundation was determined to be one of the laboratories that could satisfactorily

TABLE 1

AMPHIBOLE MASS AND SUMMARY OF ASBESTIFORM FIBER REMOVAL BY DUAL MEDIA FILTRATION

			Ontario Research Foundation			
	NWQL Amphibole Mass Number of Samples		Amphibole Fibers Number of Samples		Chrysotile Fibers Number of Samples	
Treatment Technique	Analyzed	$\leq .005$ mg/l	Analyzed	$\leq .04\times10^6$ f/l	Analyzed	$\leq 0.04\times10^6$ f/l
Filtration w/o Sedimentation						
Alum & Nonionic Polymer (985N) 2 gpm/sq ft	3	3	3	2	3	0
Alum & Nonionic Polymer (N-17 or 985N) ∿4 gpm/sq ft	5	4	10	9	10	0
Alum & Nonionic Polymer (985N) 6-8 gpm/sq ft	-	-	3	2	3	0
$FeCl_3$ & Cationic Polymer (C-31) 4 gpm/sq ft	-	-	2	2	2	1
Filtration w/ Sedimentation Tube Settlers 4 gpm/sq ft						
Alum & Nonionic Polymer (985N)	12	12	12	12	12	1
$FeCl_3$ & Nonionic Polymer (985N)	2	1	2	2	2	0

TABLE 2

AMPHIBOLE MASS AND SUMMARY OF ASBESTIFORM FIBER REMOVAL BY MIXED MEDIA FILTRATION

Treatment Technique	NWQL Amphibole Mass Number of Samples		Ontario Research Foundation Amphibole Fibers Number of Samples		Ontario Research Foundation Chrysotile Fibers Number of Samples	
	Analyzed	$\leq .005$ mg/l	Analyzed	$\leq .04 \times 10^6$ f/l	Analyzed	$\leq 0.04 \times 10^6$ f/l
Chemicals Added to Mixing Chamber						
Alum & Nonionic Polymer 4 gpm/sq ft (985N)	1	1	1	1	1	0
Chemicals Added to Two Flash Mixers						
Alum & Nonionic Polymer 4 gpm/sq ft (985N)	9	9	9	9	9	5
Alum & Nonionic Polymer 2 gpm/sq ft (985N)	1	1	1	1	1	0
Alum & Anionic & Cationic Polymer (A-23 & Catfloc B or C-31) 4 gpm/sq ft	2	2	2	2	2	0
Alum & Anionic & Nonionic Polymers (A-23 & 985N) 4 gpm/sq ft	2	2	2	2	2	0
In-Line Mixers						
Alum & Nonionic Polymer 4gpm/sq ft (985N)	1	1	1	1	1	1

Table 2 (continued)

Treatment Technique	NWQL Amphibole Mass Number of Samples Analyzed		Ontario Research Foundation Amphibole Fibers Number of Samples Analyzed		Chrysotile Fibers Number of Samples Analyzed	
		$\leq .005$ mg/1		$\leq .04 \times 10^6$ f/1		$\leq 0.04 \times 10^6$ f/1
Alum & Nonionic & Anionic Polymers (985N & A-23) 4 gpm/sq ft	2	2	2	2	2	1
Alum & Anionic & Cationic Polymers (A-23 & C-31) 4 gpm/sq ft	1	1	1	1	1	
Alum & Nonionic Polymer 6 gpm/sq ft (985N)	2	2	2	2	2	0
Alum & Cationic Polymer 4 gpm/sq ft (C-31)	1	1	1	1	1	0

TABLE 3

SUMMARY OF AMPHIBOLE MASS AND ASBESTIFORM FIBER REMOVAL BY MIXED MEDIA FILTRATION

			Ontario Research Foundation			
	NWQL Amphibole Mass Number of Samples		Amphibole Fibers Number of Samples		Chrysotile Fibers Number of Samples	
Treatment Technique	Analyzed	$\leq .005$ mg/l	Analyzed	$\leq .04 \times 10^6$ f/l	Analyzed	$\leq .04 \times 10^6$ f/l
Pressure Filtration Two-Step Precoat 1 gpm/sq ft						
Anionic Polymer (A-23) to 2nd Step of Precoat, Alum & Soda Ash to Body Feed	1	1	1	1	1	1
Alum & Soda Ash to 2nd Step of Precoat	6	6	6	3	6	1
Alum & Soda Ash to 2nd Step of Precoat and to Body Feed	3	3	3	3	3	0
Cationic Polymer to Raw Water (Catfloc B)	5	5	5	5	5	2
Alum & Soda Ash to 2nd Step of Precoat. Cationic Polymer (Catfloc B) to Raw Water	3	3	3	3	3	0
Vacuum Filtration One Step Precoat 1 gpm/sq ft						
Anionic Polymer (A-23) to Precoat	2	1	3	2	3	1

Table 3 (continued)

Treatment Technique	NWQL Amphibole Mass Number of Samples Analyzed	NWQL Amphibole Mass Number of Samples ≤.005 mg/1	Ontario Research Foundation Amphibole Fibers Number of Samples Analyzed	Ontario Research Foundation Amphibole Fibers Number of Samples ≤.04x10⁶ f/1	Ontario Research Foundation Chrysotile Fibers Number of Samples Analyzed	Ontario Research Foundation Chrysotile Fibers Number of Samples ≤.04x10⁶ f/1
Vacuum Filtration Two Step Precoat 1 gpm/sq ft						
Anionic Polymer (A-23) to Total Precoat	-	-	1	1	1	0
Anionic Polymer (A-23) to 2nd Step of Precoat	1	0	1	1	1	1
Anionic Polymer (A-23) to 2nd Step of Precoat, Alum & Soda Ash to Body Feed	5	4	5	5	5	1
Alum & Soda Ash to Second Step of Precoat	2	2	2	0	2	0
Alum & Soda Ash to 2nd Step of Precoat and to Body Feed	2	2	3	2	3	0
Cationic Polymer (Catfloc B) to Raw Water	1	1	3	3	3	0
Alum & Soda Ash to 2nd Step of Precoat Cationic Polymer (Catfloc B) to Raw Water	4	4	4	4	4	0

analyze water samples for asbestiform fibers. Thus, ORF became a subcontractor for the filtration research conducted by Black and Veatch.

One factor which must be considered when interpreting EM fiber analysis data is the meaning of the detection limit. When ORF found zero fibers in ten fields, the reported result was below detectable limits (BDL), not zero. Depending on the circumstances of the individual analysis, such as sample volume initially filtered, ORF reported a number of BDL limits from 0.02 x 10^6 f/l to 0.07 x 10^6 f/l. Most of the time the detection limit was reported as 0.02 x 10^6 f/l although early in the work 0.04 x 10^6 f/l was frequently reported.

McFarren[10] uses an intermediate category, not statistically significant (NSS) between BDL and reportable fiber counts. The NSS finding is applied to observation of less than 5 fibers in 20 fields. This would correspond to about two fibers in 10 fields for ORF. The rationale for use of NSS is that fiber counts become less reliable as fewer fibers are found. The standard deviation varies as $1/\sqrt{n}$, where n is the number of fibers found.[11] Thus the standard deviation is 10% when 100 fibers are found, and 100% when 1 fiber is found.

For the EM work done by ORF on this project, the finding of two fibers in 10 fields usually represented 0.04 x 10^6 f/l. Since the goal of the research was the "virtually complete removal," 0.04 x 10^6 f/l and lower were considered not statistically significant, and the research goal was considered to have been attained when filtered water fiber counts were 0.04 x 10^6 f/l or lower.

It is apparent from the data in Tables 1-3 that amphibole asbestiform fibers could be readily removed by filtration. Additional evidence to confirm the efficacy of filtration is found in the amphibole mass data. Many of the filter runs that were sampled contained 0.005 mg/l or less in the filter effluent. Based on the amphibole mass concentration in the raw water, this represented amphibole mass reductions of ten-fold to forty-fold or more.

Some of the variables considered in the research are to be found in Tables 1-3. Table 1 contains fiber removal data for dual media granular filters only. There is nothing in Table 1 that indicates that sedimentation before filtration was beneficial for amphibole or chrysotile fiber removal. For the treatment of clear Lake Superior water, direct filtration performed as well as filtration with sedimentation.

Ferric chloride appears to be effective for fiber removal, but alum and nonionic polymer were used in most tests because that was the combination of treatment chemicals that gave the desired combination of very low effluent turbidity and longer filter runs. This is explained in more detail by Robinson et al.

Research results for mixed media filtration are summarized in Table 2. A comparison of Tables 1 and 2 shows that mixed media filtration after two-stage flash mix was more effective for chrysotile removal than dual media filtration after one-stage flash mix, when alum and a nonionic polymer were used. With the one-stage flash mix arrangement, polymer was added at the flocculation chamber. Since two variables were changed at once, it is difficult, if not impossible, to decide which affected fiber removal more.

Another variable studied in the mixed media system was three-stage rapid mix. The purpose of the triple mix was to add and mix sequentially three conditioning chemicals, anionic polymer, alum, and cationic or nonionic polymer, with the objective of establishing, at different times in the treatment process, environments in which positive, and then negative, surface charges predominated. Unfortunately, two chemicals were added to a common barrel (mixing chamber) in the propellor type flash mixed system, so valid data were obtained only for in-line mixers. The results of three-stage rapid mixing are encouraging for both amphibole and chrysotile removal.

Diatomite filtration for asbestiform fiber removal may appear to be less successful than granular filtration, but this is not the case. More operational variations were tried with diatomite, and some were not successful. Some successful techniques were found, however, and these are found in Table 3.

Effective filtration techniques for removal of amphibole mass and fibers were the following:

a. alum conditioning of both precoat and body feed;

b. precoat conditioning with anionic polymer and body feed conditioning with alum;

c. conditioning of the raw water with Catfloc B and in some cases, alum conditioning of the precoat also.

Diatomite filtration techniques most effective for removal of both chrysotile and amphibole involved the following:

d. conditioning of precoat with anionic polymer and conditioning of body feed with alum;

e. conditioning of raw water with Catfloc B.

The treatment scheme in case d involved both negative (anionic polymer) and positive (alum coated DE) charges. A system in which Catfloc B was added to raw water before filtration through unconditioned DE would also involve both positive (Catfloc B) and negative charge systems, since diatomite ordinarily has a negative surface charge.[2] However, plain diatomite probably would not be as electronegative as diatomite coated with an anionic polymer.

Experiments with anionic polymers were conducted because of a fundamental difference in chrysotile and amphibole. Parks[12] summarized the work of numerous investigators in an article on the isoelectric point or zero point of charge of complex oxide minerals in water. The zero point of charge, or pH at which there is no net charge on the particle, is in the pH 10-11 range for chrysotile, but it is pH 5 for cummingtonite (an amphibole). In the 7-8 pH range used in filtration tests at Duluth, chrysotile would have a positive surface charge while cummingtonite, like clays and most bacteria, would be negative. It follows that in order to overcome the surface charges of both amphibole and chrysotile, it would be necessary to use treatment chemicals carrying positive and negative surface charges, respectively. The treatment chemicals should be introducted to the water separately so that the coagulation is not confined to reaction between only the treatment chemicals.

It would be logical to ask why amphibole and chrysotile fibers do not coagulate themselves since they are of opposite surface charge. A probable answer is that there are so few present, even when the concentration is 10^6 f/l. For example, if a liter of water contained 10^6 chrysotile fibers with 0.04 μm diameter and 1 μm length, the total volume of fibers would be $\sim 10^{-9}$ l or 0.001 microliter. Also, 10^6 amphibole with 0.2 μm diameter and 1 μm length would occupy a volume of 3×10^{-8} l or 0.03 microliters.

The addition of polymers to raw water in this work should have resulted in molecular concentrations on the order of 10^{14} to 10^{16} molecules per liter, depending upon the dose and molecular weight of the polymer, and assuming that every polymer molecule was a separate entity (the same assumption made for asbestiform fibers).

It is obvious that polymer molecules very greatly outnumber (by a factor of 10^8 to 10^{10}) asbestos particles, so the chances for a polymer-fiber collision would be much better than for a fiber-fiber collision. Thus polymer conditioning is needed for fiber removal, and since surface charges differ with type, different polymers are needed to remove amphibole and chrysotile.

One other factor that may be related to fiber removal or, conversely, to the ability of fibers to pass through filters, is fiber size. For all filters, the typical size of chrysotile fibers in the effluent was smaller than the typical size in the raw water. This size relationship was also true for amphiboles in DE filtrate. Because only 25 amphibole fibers were observed and sized for granular media tests, this small sample was more subject to distortion by a typical fibers and was not very suitable for a chi-square analysis. The factor of particle size is probably less important than surface charge, since particles in the water, both before and after filtration are in the size range (∿1 μm) suggested by Yao[13] to have minimum removal efficiency by granular filtration.

Filtration results can be summarized briefly. The methods found more effective than others for removal of both amphibole and chrysotile were mixed media filtration employing alum and an anionic polymer and two-stage flash mixing; and pressure diatomite filtration employing Catfloc B added to the raw water and no conditioning of the DE. Methods showing potential for further research are three-stage flash mixing with sequential addition of anionic polymer, alum, and cationic or nonionic polymer, followed by flocculation and filtration; and pressure DE filtration with anionic polymer conditioning of the precoat and alum conditioning of the body feed.

b. Efforts to Develop Rapid Detection Methods

A limited effort to learn about rapid detection of asbestiform fibers was made in this research, but the principal objective was to learn about fiber removal by filtration. Other efforts to develop a rapid fiber detection method are underway, sponsored by EPA and other Federal agencies. One method being investigated involves placing a water sample in a laser light beam measuring scattered light from incident angles of about 10° to 135°, and relating variations of light intensity and incidence angle to the types of particles present in water. One of the goals of these efforts is to provide a technique that is practical for monitoring both amphibole and chrysotile asbestiform fibers in water at filtration plants. Such a technique should be rapid enough to permit a plant operator to make meaningful changes in the treatment process in order to hold fiber content of the filtered water to a minimum. Until a more rapid method is available, water filtration plants on Lake Superior should use the x-ray diffraction method, along with occasional EM analyses.

6. Future Research

Information developed in this pilot plant research permits a number of questions to be formulated for future study. Among the ideas that could be investigated are the following:

a. Ways to improve chrysotile removal by anionic polymer conditioning of DE or by the use of three-stage mixing and combination of three conditioning chemicals in granular filtration.

b. Effect of high algal counts on filter performance.

c. Fiber removal during times of highest amphibole mass and fiber count.

d. Verification of POPO optimization of diatomite filtration.

e. Additional filtration experiments at 5 to 6 gpm/ft with granular filters.

f. Effect of mixing intensity on filtration, and a comparison of back-mixing vs. in-line mixing.

g. Further laboratory development, followed by pilot plant tests, of an operator's method for monitoring the presence of asbestiform fibers in water.

A number of the suggestions for future work represent an extension of past work into promising study areas. Additional research is needed to increase the knowledge of the water treatment profession on the topic of asbestiform fiber removal by filtration.

7. Conclusions

a. No discernible tie was evident between the Duluth raw water turbidities and the asbestiform fiber levels.

b. At finished water turbidities of less than 0.1 TU, the amphibole fiber count and mass determinations were usually below the detection limits of the analytical method used.

c. A general association was indicated between the NWQL amphibole mass concentration and the ORF amphibole fiber counts in the Duluth raw water.

d. No relationship was observed between the counts of the amphibole and the chrysotile fibers in the Duluth raw water.

e. Based on achieving BDL or near it, 32 of 34 MM-2 (granular) runs and 21 of 23 MM-1 runs were successful for amphibole removal. Only 8 of 34 MM-2 runs and 2 of 23 MM-1 runs were successful for chrysotile removal. Alum and nonionic polymer worked best in granular filters.

f. Amphibole fiber removal accomplished by the tri-media filter exceeded that accomplished by the dual media filters and the DE filters.

g. For the pressure DE tests, 19 of 27 were successful for amphibole removal, but only 4 of 27 were successful for chrysotile removal. Vacuum DE filtration (BIF) was not found suitable for treating the raw water being tested.

h. A medium grade precoat and a fine grade body feed were most effective in turbidity and asbestiform fiber removal by DE filtration.

i. For the Duluth raw water, two treatment conditions, alum coated or plain precoat, with a cationic polymer introduced to the raw water, and an anionic polymer added to the precoat and alum coated body feed were most effective in turbidity and asbestiform fiber removal filtration.

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The following EPA personnel contributed to this report:

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9. References

1. Robinson, J.H., et al., Direct Filtration of Lake Superior Water for Asbestiform Solids Removal. Presented at Annual Conference, American Water Works Association, Minneapolis, Minnesota (1975).

2. Baumann, E.R., Diatomite Filter for Asbestiform Fiber Removal from Water. Presented at Annual Conference, American Water Works Association, Minneapolis, Minnesota (1975).

3. Direct Filtration of Lake Superior Water for Asbestiform Fiber Removal. By Black and Veatch, Consulting Engineers, U.S. Environmental Protection Agency, National Environmental Research Center - Cincinnati, Water Supply Research Laboratory (April 1975). Summary Report #EPA 670/2-75-050a and six appendices #EPA 670/2-75-050b to EPA 670/2-75-050g.

4. *Standard Methods for the Examination of Water and Wastewater. APHA, AWWA, WPCF, New York (13th Edition 1971).*

5. Cook, Philip M., Semi-quantitative Determination of Asbestiform Amphibole Mineral Concentrations in Western Lake Superior Water Samples. Proc. 23rd Annual Conference on Applications of x-ray Analysis, Denver, Colorado (1974).

6. Chatfield, E.J. and Pullen, H., Measuring Asbestos in the Environment. *Canadian Research and Development*, 7:6:23 (Nov.-Dec. 1974).

7. Carter, Robert E., Private Communication to Mr. O. J. Schmidt.

8. Contract No. DACW 37-74-C-0079, Department of the Army, St. Paul District, Corps of Engineers (February 1974).

9. Fairless, William. Memorandum from U. S. EPA Region V to Water Supply Research Laboratory.

10. McFarren, Earl F., et al., Asbestos Analysis by Electron Microscope. Presented at Second Annual Water Quality Technology Conference, AWWA, Dallas, Texas (1974).

11. Chatfield, E.J., Private communication to Mr. O. J. Schmidt.

12. Parks, George A., Aqueous Surface Chemistry of Oxides and Complex Oxide Minerals. Symposium on Equilibrium Concepts in Natural Water Systems, Proc. 151st Meeting Am. Chem. Soc. Pittsburgh, Pa. (1966). published as *Equilibrium Concepts in Natural Water System*, W. Stumm, ed., (1967), p. 121.

13. Yao, K., et al., Water and Waste Water Filtration: Concepts and Applications. *Environmental Science and Technology*, 5:11:1105 (November 1971).

APPENDIX VII

HEALTH EFFECTS CAUSED BY EXPOSURE TO DRINKING WATER CONTAMINANTS

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HEALTH EFFECTS CAUSED BY EXPOSURE TO DRINKING WATER CONTAMINANTS

The following sections on the toxicity of organics and inorganics found in drinking water reflect the views of the respective authors of those sections and not necessarily the views of the Environmental Protection Agency. These reports provide necessary preliminary information with which to assess the health effects of these contaminants and will be carefully reviewed along with other investigations, such as that of the Science Advisory Board, in future discussions.

A. TOXICITY OF ORGANICS PRESENT IN DRINKING WATER

1. Introduction

Over the years, the occurrence of organic materials in all tap water has been acknowledged almost universally. Until relatively recently, data describing such occurrence has been almost exclusively the result of gross measurements such as carbon-chloroform-extracts and non-volatile-total organic-carbon. The advent and application of more sophisticated analytical tools, such as the mass spectrometer, has led to the conclusive identification of some of the organic components of drinking water. Appendix I is the most recent compilation of compounds that have been found in various potable supplies. Recent estimates by the Water Supply Research Laboratory of E.P.A. indicate that of all the compounds present the identified compounds may account for no more than 10 percent by weight.

The compounds in Appendix I are not all unique to drinking water. Concurrent exposure by various segments of the U.S. population exists via some foods, ambient air, occupational environment, and/or household products (e.g., over-the-counter medications, cleaning solutions, and cosmetics). For some compounds, particularly some of those suspected of being by-products of chlorination of tap water (e.g., dibromochloromethane and bromodichloromethane), man's exposure is restricted solely to potable water and to foods processed with that water.

Many factors enter into the hazard/safety evaluation of organics in drinking water. Among them is determination of the toxicity of the materials to which man is exposed. Toxicity data include a broad range of biological parameters, a few of which are listed below:

1. the amount of material required for the production of acute illness and mortality;

2. the ways in which a compound is handled metabolically by the body;

3. the types of diseases and specific organs affected from repeated exposures for a part or all of the lifespan;

4. the reversability or irreversability of the lesions;

5. the particular groups of the populations that might be at greater risk to intoxication; and

6. the factors, both endogenous and exogenous, that alter the toxicity of foreign compounds and/or compromise the organism's ability to respond to insults from foreign compounds.

The central objective from the investigations of such questions is the identification of what will occur in man through the utilization of predictive experimental animal models. Well designed and closely controlled experimentation can yield information valuable in protecting man against exposure to hazardous doses of a chemical or mixture of compounds. Epidemiologic surveillance can monitor body burdens and health status as a function of exposure levels and durations of exposure to insure against the possibility of incorrect extrapolations and to guard against the unexpected sensitivity in population subsets.

2. Acute Toxicity

Data on acute doses required for intoxication serve, first, as a yardstick against which to compare one compound with another and, second, as a starting point in the design of repeated exposure and metabolism studies. The comparative evaluations of acute toxicity have been formalized into a rating system (1) which is described in Table 1.

The compounds listed in Appendix I underwent a literature search to find data on acute toxicity and to categorize the relative toxicities according to the rating system of Gleason et. al. (1). Table 2 displays the results of this evaluation. Most of the compounds for which data are available are in the categories "moderate" and "very" toxic. For 30 percent of all the compounds, no acute toxicity data were available from which to assign a rating.

While individual compounds are usually rated for their acute toxic potential, mixtures of these agents can be similarly classified. Tardiff and Deinzer (2) reported that extracts of organics from drinking water were tested in mice and found to have LD_{50} values that classified the mixtures as "very" toxic. The mixtures represented approximately 30 percent of the organics originally present in the tap water samples used.

It should be remembered that acute toxicity measurements for these contaminants are based upon doses that are far greater than those encountered from drinking water. Acute toxicity does not necessarily bear any relationship to chronic toxicity which is more relevant to low-level

TABLE 1

CLASSIFICATION SYSTEM FOR ACUTE TOXICITY OF CHEMICALS (1)

Toxicity Rating or Class	Probable Lethal Dose for Man or LD_{50} for Experimental Animals
6 - Super Toxic	less than 5 mg/kg
5 - Extremely Toxic	5 to 50 mg/kg
4 - Very Toxic	50 to 500 mg/kg
3 - Moderately Toxic	500 to 5000 mg/kg
2 - Slightly Toxic	5 to 15 gm/kg
1 - Practically Non-toxic	greater than 15 gm/kg

TABLE 2

ACUTE TOXICITY RATINGS OF COMPOUNDS IDENTIFIED IN DRINKING WATER

Toxicity Rating	Number of Compounds
6 - Super Toxic	1
5 - Extremely Toxic	7
4 - Very Toxic	47
3 - Moderately Toxic	62
2 - Slightly Toxic	11
1 - Practically Non-toxic	3
Unknown..	56

human exposure to organic chemicals in drinking water. The following section discusses chronic toxicity.

3. Chronic Toxicity/Carcinogenicity

Exposure to repeated small quantities of environmental chemicals suggests a greater possibility of chronic, rather than acute, intoxication. One of the more serious irreversible expressions of chronic toxicity is carcinogenesis. Because of the nature of the disease, chemically-induced carcinogenesis is considered one of the more dread toxic properties. However, an entire spectrum of chronic--but non-neoplastic--diseases can be equally serious personal and societal tragedies. Attention must be focused on all forms of chronic illness whose etiology is environmental agents.

The determination that a compound at ambient concentrations is or is not a tumorgenic risk to man is a relatively difficult task as acknowledged by scientists of the National Cancer Institute. The observation of a neoplastic response in an experimental species from exposure to a chemical invokes many questions. Perhaps one of the most significant questions concerns whether the animal model in which the carcinogenic expression was observed is predictive of the same response in man. Thus, of itself, a chemical may be a carcinogen in an experimental species (e.g., the mouse); however, the same chemical may not necessarily be a carcinogenic hazard to man. It must be emphasized that such a model can be validated by specific and definitive studies, but that such studies may not have been performed at the time the neoplastic response is discovered.

In an effort to take into account all factors that enter into the evaluation of a compound's carcinogenic property, operational definitions were generated by the Water Supply Research Laboratory of E.P.A. with assistance from the National Cancer Institute. Those definitions are listed in Table 3. The definitions reflect the necessity to make reliable and accurate judgments about the agents. Thus, relatively few compounds meet the criteria for "positive" carcinogen as exemplified by the brevity of the list of occupational carcinogens (OSHA list of 14 compounds). However, many more compounds are classified as "suspect" carcinogens because of the lack of sufficient and appropriate information from which to definitely predict or acknowledge the hazard to man. (Acknowledgment of the effect via human data is never a goal with respect to cancer but may be a reality because of accidents or misjudgments.)

Preceding considerations were related only to qualitative aspects of carcinogenesis: Is a compound a carcinogen or not? Is it a carcinogenic hazard to man or not? Such a consideration excludes the concept of potency; namely, how potent is one compound vs. another in the induction of tumors. Stated differently, potency involves how much of a compound and how long an exposure are required to develop tumors in a defined population. For some time, oncologists have spoken of "strong" and

TABLE 3

CLASSIFICATION SYSTEM AND CRITERIA FOR THE DEFINITION OF CARCINOGENIC PROPERTIES OF CHEMICALS*

Class #1 - Positive or Recognized Carcinogen

Criteria:
- a. On an acceptable list of human carcinogens (e.g., the OSHA list)
- b. Strong experimental evidence - many species and strains, etc.
- c. Strong evidence or strong suspicion as to cause and effect in man

Class #2 - Suspect, Possible or Potential Carcinogen

Criteria:
- a. Structure similar to proven carcinogen
- b. Positive response in one species
- c. Mutagencity data
- d. No epidemiologic evidence
- e. Either not tested or tests inadequate

Class #3 - Unknown Carcinogenic Potential

Criteria:
- a. Tests limited in time
- b. Tests limited in dose schedule
- c. Insufficient number of animals
- d. Route of administration not relevant
- e. Improper species and/or strain used
- f. Dose schedule not relevant: strong overlay of toxicity
- g. Role of contaminants
- h. Not tested & no structure-activity suspicion

Class #4 - Negative or Non-carcinogenic

Criteria:
- a. Repeated tests in many species and strains
- b. Adequate protocols
- c. Confirmed in several laboratories
- d. Established non-carcinogenic in the absence of contaminants
- e. Strong epidemiologic evidence that it is non-carcinogenic in man

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* System developed in collaboration with the National Cancer Institute.

"weak" carcinogens implying a difference in dose to obtain the same effects (e.g., 50 percent tumor formation). If, for example, a compound at environmental levels requires 100 years of exposure to induce tumor formation in man, this compound may be regarded as a relatively small cancer hazard to society as compared to one which requires only a decade to obtain a similar response. Although the regulatory agencies will wish to exercise control over all carcinogenic substances within their respective jurisdictions, consideration of potency may assist in establishing priorities for control measures and for allocation of resources.

The recognition of the tumor-inductive property of chemicals led to a cursory examination of biological literature to determine the evidence, both positive and negative, for carcinogenic responses induced by the chemicals identified in tap water (Appendix I). The results of this evaluation are listed in Table 4. The "positive" or known carcinogens are aldrin, benzene, benzopyrene, carbon tetrachloride, DDT, 2,4-dichlorophenol, dieldrin, and 2,4-dimethyl phenol.

The "negative" or non-carcinogens are acetic acid, acetone, barbital, benzoic acid, ethanol, and methanol. Of the 187 compounds, there was no data and insufficient structure-activity information to make a judgment of 137 chemicals (i.e., over 70 percent of those found to have been present in tap water and to which some humans were exposed). It must be concluded that although more information must be obtained on "suspect" carcinogens, a great deal more experimental evidence must be learned about the chronic toxicity of a substantial number of compounds. Continued search for additional chronic toxicity data may yield additional pertinent information on these compounds.

A few studies (3-5) have been reported in which organic mixtures extracted from drinking water were administered repeatedly to determine carcinogenic potential. The results indicated that, in mice, carbon extracts elicited neoplastic responses when injected but not when ingested (3,4). In another investigation (5), injections of carbon extract of organics from drinking water failed to induce tumor formation.

TABLE 4

CARCINOGENICITY CLASSIFICATION OF COMPOUNDS IDENTIFIED IN DRINKING WATER

Class	Number of Compounds
1 - Positive	8
2 - Suspect	35
3 - Unknown	138
4 - Negative	6

4. Ongoing Research

The Water Supply Research Laboratory of E.P.A. is actively engaged in investigating the toxicity of organics in drinking water for the purpose of identifying hazards and risks to man's health via this mode of exposure and of determining, if no hazard exists, the magnitude of the margin of safety from environmental exposures.

Toxicologic experimentation on the organics in drinking water is guided by Principles for Evaluating Chemicals in the Environment (6).

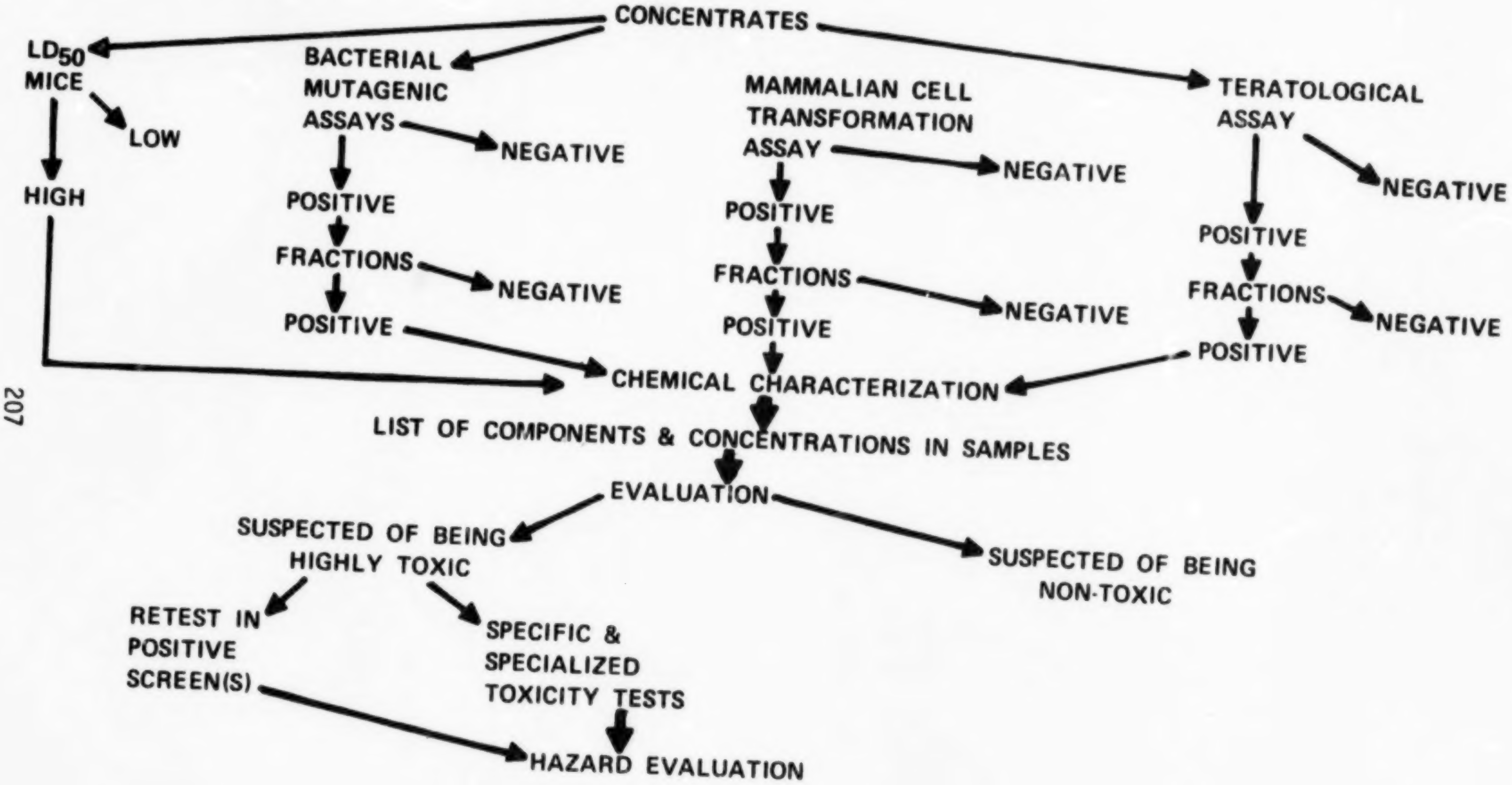
A two-pronged approach is being used to investigate the organics in tap water. The first studies the biological effects of individual compounds. The second is aimed at the elucidation of the toxic properties of mixtures of organics which are present in tap water.

Several classes of compounds identified in potable water are under active investigation with regard to their toxicity in experimental animals. These classes include the chlorinated ethers, the chlorinated and brominated benzenes, and the halogenated methanes. Investigations are designed (1) to determine the most significant animal model through studies of comparative metabolism and (2) to uncover pathologic changes resulting from varying levels of repeatedly administered compounds in appropriate experimental species.

The chloro-ethers of immediate interest are bis(2-chloroethyl) ether and bis(2-chloroisopropyl) ether. The metabolism of these agents is being studied in several species including sub-human primates in order to determine the species that most closely resembles man in its metabolism so that additional toxicity studies may be performed in a species that is more predictive of man's response. Base-line data are being obtained on the effects from single and relatively short-term repeated exposures in one classical model. A specialized model is being utilized to determine possible carcinogenic potential. Investigations have been designed to establish any mutagenic activity that might be of concern to man. Because very little is known of the toxicity of these compounds (although they are chemically related to a potent toxicant and carcinogen), a broad scope of experimentation is required on these compounds.

Halogen-substituted benzenes demonstrate a relatively long biological half-life that suggests accumulation in the body with repeated exposures with consequent chronic toxicity. Because of evidence suggesting the acute alteration of zenobiotic metabolism, these compounds are being studied to determine their potential interaction with other foreign compounds to alter toxicity (e.g., synergistic responses). The entire homologous series of chlorine- and bromine-substituted benzenes are under investigation.

FIGURE 1. PROTOCOL FOR TOXICITY SCREENING OF ORGANIC CONCENTRATES FROM DRINKING WATER


CONCENTRATES
LD50 MICE
LOW
HIGH
BACTERIAL MUTAGENIC ASSAYS
NEGATIVE
POSITIVE
FRACTIONS
NEGATIVE
POSITIVE
MAMMALIAN CELL TRANSFORMATION ASSAY
NEGATIVE
POSITIVE
FRACTIONS
NEGATIVE
POSITIVE
TERATOLOGICAL ASSAY
NEGATIVE
POSITIVE
FRACTIONS
NEGATIVE
POSITIVE
CHEMICAL CHARACTERIZATION
LIST OF COMPONENTS & CONCENTRATIONS IN SAMPLES
EVALUATION
SUSPECTED OF BEING HIGHLY TOXIC
SUSPECTED OF BEING NON-TOXIC
RETEST IN POSITIVE SCREEN(S)
SPECIFIC & SPECIALIZED TOXICITY TESTS
HAZARD EVALUATION

Halogenated methanes (dibromochloromethane and bromodichloromethane) are possible chlorination by-products for which there is presently no toxicity information. A broad spectrum of experimentation is planned including comparative metabolism and comparative toxicity with special emphasis on chronic toxicoses.

The investigation of the toxicity of mixtures of organics from tap water is described schematically in Figure 1. Extracts or concentrates of organics from municipal water supplies can be screened with biological systems to determine what types of toxicity problems to investigate further and to establish which water supplies may have the greater potential for adverse health effects.

Presently extracts are being obtained from five U.S. cities that represent the major types of water sources for drinking water. These extracts will be subjected to the four screening systems identified in Figure 1. The LD_{50} is utilized as a reference for comparison with the toxicity of known compounds and with the toxicity of other concentrates. The in vitro systems are used predominantly to predict possible mutagenic and carcinogenic expressions in vivo. The teratology assay is performed in whole animals and indicates the ability to induce birth deformities.

Positive responses in any of the screening assays initiate an attempt to isolate the effects in subfractions of the extracts. By isolating a few fractions with biological activity, it is then more feasible to identify the constituents within the active fractions rather than in the entire concentrate.

Chemical identification of components requires a reconfirmation of the pure agent in the positive screens. Subsequent to reconfirmation, the active compounds are subjected to more definitive investigations for ultimate evaluation of impact on man.

Throughout these investigations, substantial efforts are expended in coordination and collaboration with scientists and administrators of other federal agencies such as the National Cancer Institute, the Food and Drug Administration, and the National Institute of Environmental Health Sciences. Through such interactions, governmental resources are maximally utilized for the benefit of the citizens.

5. References

(1) Gleason, Marion N., Gosselin, Robert E., Hodge, Harold C., and Smith, Roger P. Clinical Toxicology of Commercial Products: Acute Poisoning. 3d ed. Baltimore, Williams and Wilkins, Co., 1969.

(2) Tardiff, Robert G. and Deinzer, M. "Toxicity of organic compounds in drinking water." In: Proceedings of 15th Water Quality Conference, Feb. 7-8, 1973, University of Illinois, pp. 23-37.

(3) Hueper, W. C. and Payne, W. W. "Carcinogenic effects of raw and finished water supplies." Amer. J. Clin. Path. 39(5):475-81. May 1963.

(4) Hueper, W. C. and Ruchoft, C. C. "Carcinogenic studies on adsorbates of industrially polluted raw and finished water supplies." Arch. Ind. Hyg. Occup. Med. 9:488-95, 1954.

(5) Dunham, Lucia J., O'Gara, Roger W., and Taylor, Floyd B. "Studies on pollutants from processed water: collection from three stations and biologic testing for toxicity and carcinogenesis." Amer. J. Public Health 57(12):2178-85, December 1967.

(6) Principles for Evaluating Chemicals in the Environment. Washington, D.C., National Academy of Sciences, 1975.

B. TOXICITY OF INORGANIC CHEMICALS PRESENT IN DRINKING WATER

1. Introduction

Because of health effects concerns the concentration of several inorganic chemicals are limited in drinking water. Limits for arsenic, barium, cadmium, chromium, cyanide, fluoride, lead, mercury, nitrate, selenium, and silver have been proposed and published in the Federal Register (1) under provisions of P.L. 93-523: Safe Drinking Water Act.

In the 27-year period 1946-1973, there were 405 waterborne disease outbreaks but only 10 of these outbreaks were related to inorganic chemical poisonings. Deaths were more likely to be associated with these chemical-caused outbreaks; seven deaths occurred as well as 210 cases of illness (2). Cancer has not been attributed to have been caused by contamination of drinking water with inorganic chemicals in this country.

None of the inorganic chemicals have been limited in drinking water because the chemical was considered to be a carcinogen but for several of the chemicals (arsenic, cadmium, chromium, nitrate, and selenium) consideration was given to data concerning carcinogenic effects. Beryllium and nickel are not limited in drinking water but are two additional metals that should be considered for carcinogenic effects.

2. Arsenic

In certain parts of the world the high levels of arsenic found in drinking water have been associated with a high rate of arsenicism and skin cancer in the population (3). Tseng et. al. (12) reported a geographical correlation in Taiwan between levels of arsenic exposure in well water and the frequencies of skin cancer, hyperpigmentation, Keratosis, and a peripheral vascular disorder (Blackfoot disease). A dose-response relationship was seen between the occurrence of skin lesions, including cancer, and the arsenic content of the water. No excessive occurrence of other cancers has been reported in areas where the water contains arsenic. The available studies consistently point to a causal relationship between skin cancer and heavy exposure to inorganic arsenic in drugs, in drinking water with a high arsenic content, or in the occupational environment.

Adequate oral studies on arsenic trioxide in the mouse and on lead arsenate, calcium arsenate, sodium arsenate, arsenic trioxide and sodium arsenite in the rat gave negative results.

It should be noted that OSHA has formally proposed a new limit for inorganic arsenic of 4 $\mu g/m^3$; the previous limit suggested by NIOSH was 50 $\mu g/m^3$ (5). The 4 $\mu g/m^3$ limit represents an arsenic intake of 40 μg

per work week. Extrapolating to water exposure the 40 μg/week of arsenic would represent a 4 μg/liter intake for water. Applying a safety factor of 100, the comparable drinking water standard would be 0.04 μg/l.

Arsenic has usually been considered a geochemical contaminant and high concentrations have been noted in ground water in selected areas of the southwest and northwest of the country. Water supplies exceeding the limit of 0.05 mg per liter are located in California, Oregon, and Nevada. Arsenic was related to five, or half of the inorganic chemical-caused water poisonings in the past 27 years, and the reasons for these poisonings are most varied. One outbreak of ten cases and three deaths resulted when an arsenical weed killer was dumped into a well in West Virginia. These are the only murders that have been noted in the review of waterborne outbreaks. Two outbreaks concerned the back-siphonage of arsenic compounds into water supplies, and there were five cases of illness and four deaths resulting. Recently, a well was drilled at a new factory site in Minnesota and people working there became ill (10). Arsenic was detected in their blood and investigation revealed arsenic in the well water of 11.8 - 21 mg/liter. The site had been used to mix grasshopper bait many years before and it is likely that some unused pesticide had been buried where the well was drilled. Two girls in a Nevada family became ill and, after some difficulty of diagnosis, it was determined that they had arsenic poisoning. The well at the family ranch varied between 0.5 - 2.75 mg/liter of arsenic from natural causes.

Health effects research planned for arsenic includes a study of body burden in areas where arsenic is high in drinking water. The mutagenicity of arsenic will be determined by use of cultured mammalian cells.

3. Beryllium

Bone and lung cancers have been produced experimentally in animals and 20 malignant tumors have been recorded among the 735 cases of beryllium disease; however, the available evidence was not considered sufficient to positively incriminate beryllium as a carcinogen in humans (6). Beryllium is classified as an experimental carcinogen by the American Conference of Government Industrial Hygienists (7). They define an experimental carcinogen as industrial substances found to be capable of inducing tumors under experimental conditions in animals and have established a TLV of 0.002 mg/m^3 of air.

Beryllium will be tested for mutagenicity in a cultured mammalian cell test system.

4. Cadmium

Several studies suggest that occupational exposure to cadmium oxide may increase the risk of prostate cancer in man but the size of the groups studied was considered small (3). It was recently reported that there was an increased risk of death due to malignant neoplasms in a study of 283 cadmium smelter workers (5). No data are available to suggest that non-occupational exposure to cadmium constitutes a carcinogenic hazard. Studies of rats and mice showed that a level of 5 mg/l cadmium acetate given in drinking water until death did not significantly increase the incidence of tumors (3). The estimated intake of cadmium from drinking water is 3 µg per day (1).

Health effects research currently being conducted and planned is in regard to the possible role of cadmium in hypertension and cardiovascular disease. The mutagenicity of cadmium will be tested in a cultured mammalian cell test system. The relative bioavailability of cadmium in water as opposed to cadmium in foodstuffs is also being determined.

5. Chromium

There is an excessive risk of lung cancer among workers in the chromate-producing industry (3,4). It is likely that exposure to one or more chromium compounds is responsible, but the identity of this or these is not known. There is no evidence that non-occupational exposure to chromium constitutes a cancer hazard. The NAS reports that no harmful effects on the health of man are known to have resulted from the presence of chromium in public drinking water at current concentrations (4). Studies of rats and mice showed that a level of 5 mg/l chromic acetate given in drinking water until death did not significantly increase the incidence of tumors at various sites as compared with controls (3). The estimated intake of chromium from drinking water is 5 µg per day (1).

No health effects research is planned other than testing the mutagenicity of chromium in a cultured mammalian cell test system.

6. Nickel

There has been an excessive risk of cancers of the nasal sinus and lung among nickel refinery workers and it is probable that nickel in some form is carcinogenic (3,4). There is no evidence to suggest that non-occupational exposure to nickel constitutes a cancer hazard (3). The estimated intake of nickel from drinking water is 10 µg per day (1).

It is planned to produce a criteria document recommending a drinking water standard for nickel. The mutagenicity of nickel will be determined by use of a cultured mammalian cell test system.

7. Nitrate

Nitrate concentrations in drinking water have been limited because of the possibility of developing methemoglobinemia in infants who were fed water high in nitrate. A few community water systems exceed the nitrate limit but in many rural areas the farm wells have a very high concentration of nitrate. It has been hypothesized that in high concentrations the nitrogen might combine with amines in contaminated water or in the gastrointestinal tract to form nitrosamines, a recognized carcinogen. The development of nitrosamines has been demonstrated experimentally using much higher concentrations of nitrates or nitrites than are known to occur in water. It has been pointed out that a few counties of Texas that had nitrate-in-ground-water problems had higher cancer rates but a suitable data base for an epidemiological study was not available.

The production of nitrosamines in cured meat is being researched by other agencies. The concentrations of nitrate and nitrite are greater when these chemicals are used as a preservative of food than drinking water concentrations.

8. Selenium

In 1962 the drinking water limit was lowered to 0.01 mg per liter primarily out of concern for possible carcinogenic properties of the element. Since that time evidence has been developed indicating that selenium could both cause and prevent cancer. Several animal studies showed that tumors were developed from exposure to selenium. In the North Central and Rocky Mountain Regions of the country there are areas that are geochemically rich in selenium. Forage crops and plants in these areas often contain more than 100 parts per million of selenium. Cows, sheep, and horses in these areas may die from consuming enough selenium in forages to develop selenium toxicity. Research has shown that grain from selenium-rich areas had a higher selenium content and when used as poultry feed, it promoted the growth of chickens and turkeys. It was proposed that selenium be used as an additive to animal feed.

The Commissioner of the Food and Drug Administration reviewed the carcinogenic problem of selenium last year (11). He concluded that selenium could be safely used as an additive to swine, turkey, and chicken feed because of its nutritive value and lack of health hazard when used at prescribed concentrations. The inadequacy of the toxicological studies that produced tumors was reviewed.

Research is being conducted on the comparative availability of selenium from food and water so that a drinking water limit can be established with consideration given to intake from food. A study is planned to determine the human body burden in areas where selenium is high in drinking water. Mutagenic screening tests will also be conducted.

9. Consequences

Apparently, the inhalation exposure to fumes or dust in the industrial setting produces a very different biological effect that the ingestion exposure from food and water. An increased risk of developing cancer is not expected from consuming water contaminated with beryllium, cadmium, chromium, or nickel. There are other health effects that require limiting the concentration of these elements in drinking water.

Arsenic has been demonstrated to be a carcinogen in drinking water but may not present as serious a problem as indicated from industrial inhalation exposure. Epidemiological research should be conducted to see if a lower drinking water limit is necessary.

More information is needed on the formation of nitrosamines and on-going research should provide this. Selenium apparently does not present a cancer problem.

10. References

(1) Train, R. E. Primary Drinking Water, Proposed Interim Standards.

(2) McCabe, L. J. *Problem of Trace Metals in Water Supplies - An Overview.* Proceedings 16th Water Quality Conference, University of Illinois (1974).

(3) IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man, *Some Inorganic and Organometallic Compounds*, Volume 2, International Agency for Research on Cancer, Lyon (1973).

(4) National Academy of Sciences, *Medical and Biologic Effects of Environmental Pollutants*, Chromium (ISBN 0-309-02217-7) 1974; Nickel (ISBN 0-309-02314-9) 1975.

(5) *Toxic Materials News*, Vol. 2(7), p. 53 (1975).

(6) *Preliminary Air Pollution Survey of Beryllium and its Compounds*, USDHEW, Raleigh, North Carolina (1969).

(7) ACGIH, P.O. Box 1937, Cincinnati, Ohio.

(8) McCabe, L. J. *et. al.*, "Survey of Community Water Supply Systems." *JAWWA*, *62*(11), 670 (1970).

(9) Kopp, J. F., and Kroner, R. C., *Trace Metals in Waters of the U.S.*, Cincinnati, Ohio.

(10) Feinglass, E. J. *Arsenic Intoxication from Well Water in the United States.* New England J. Med. 288, 828(1973): Federal Register 40(51) 11990-11998 (March 14, 1975).

(11) Schmidt, A. M. *Selenium in Animal Feed*, Federal Register 39(5) 1355-1358 (January 8, 1974).

(12) Tseng, W. P., Chu, H. M., How, S. W., Fong, J. M., Lin, C. S., and Yels. Prevalance of Skin Cancer in an Endemic Area of Chronic Arsenicism in Taiwan, J. Nat. Cancer Inst. 40, 454-463 (1968).